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May 26, 1930.

I hereby recommend that the thesis prepared under my supervision by John H. Payne entitled The Mechanism of the Action of Hydrogen Peroxide upon Simple Carbon Compounds

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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A. Shipley Frye.

Henry Max Goettch

THE MECHANISM OF THE ACTION OF HYDROGEN PEROXIDE
UPON SIMPLE CARBON COMPOUNDS

A dissertation submitted in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

to the Graduate School of the
University of Cincinnati

1 9 3 0

by

JOHN H. PAYNE

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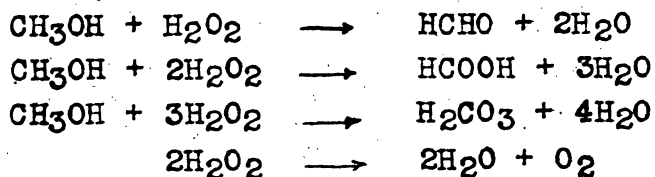
B.S. Butler University 1927
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INTRODUCTION

During the course of a series of earlier Master Thesis experiments, (1) designed primarily to determine the effect of variations in the acidity of the medium upon the oxidation of methyl alcohol by hydrogen peroxide, it was noted that the yield of oxidation products obtained was invariably greater than the theoretical yield which should have been produced by the following reactions from the given amounts of hydrogen peroxide.



That is, the yield of reaction products was found to be uniformly 107-109% of the calculated values in terms of the amounts of hydrogen peroxide used.

Since the experimental procedure was so conducted that the amount of hydrogen peroxide actually used in the reactions was definitely known, the only explanation possible was that simultaneously with the oxidation reactions, involving the hydrogen peroxide, there were other reactions involving the formation of reducing substances whose presence had escaped notice. This conclusion found its verification in the discovery that hydrogen was produced as one of the reaction products and could actually be determined quantitatively if the reaction were conducted in a closed system.

Since this unsuspected and unexplained liberation of hydrogen had not been recorded in the literature, a quantitative study of the reaction with a view to suggesting a possible reaction mechanism was initiated.

Since it is known that hydrogen is liberated by the action of hydrogen peroxide upon formaldehyde in both acidic and basic solutions, it seemed logical to assume that the hydrogen produced in the case of methyl alcohol resulted in a reaction from the intermediate production of formaldehyde as the first oxidation product. The literature regarding the quantitative nature of this reaction with formaldehyde, however, was found to be quite contradictory, making interpretation of the reaction with methyl alcohol on this basis quite impossible. Moreover there might be a possibility of the liberation of hydrogen by the action of hydrogen peroxide upon formic acid, a reaction which has been little studied. With these facts in mind, a thorough quantitative study of the reactions between hydrogen peroxide and both formic acid and formaldehyde was deemed essential to the interpretation of the reaction with methyl alcohol.

These studies led to an extensive consideration of the mechanism of the reaction between hydrogen peroxide and organic compounds of simple structure starting with the simplest compounds formic acid, formaldehyde, and methyl alcohol, and then extending to the next members of the homologous series, namely, acetic acid, acetaldehyde, and ethyl

alcohol. The reactions of all of these compounds with hydrogen peroxide, with the exception of ethyl alcohol, have been specifically studied in this research, and a general reaction mechanism to explain these reactions has been developed. Owing to a lack of time ethyl alcohol was not studied. Since, however, the mechanism developed depends upon the formation of the aldehyde by direct oxidation as the first step in the reaction, this omission is not paramount.

In the following dissertation, first there will be given a historical outline of previous work recorded in the literature on each of the compounds studied. The compounds will be discussed in the order in which their reactions were investigated in the experimental work. The historical outline will be followed by the experimental procedure and the proposed reaction mechanism as developed from the results obtained.

HISTORICAL

A. Formic Acid

Although the literature quite consistently states that formic acid is oxidized directly to carbonic acid in most instances, the conditions under which complete oxidation takes place remain quite vague. Also in no cases were the reactions conducted in an apparatus designed to collect the gaseous products of the reaction so that hydrogen could be detected and quantitatively estimated if it were one of the products.

Kastle and Loevenhart (2) state that formic acid is not attacked by hydrogen peroxide at 60° and 80°C. Since a very dilute solution of hydrogen peroxide was used, any oxidation which did take place probably remained unnoticed. Four years later the same authors (3) state that formic acid is oxidized quite readily by hydrogen peroxide at 100°C., the reaction being catalyzed by the presence of platinum. The authors were interested chiefly in measuring the speed of the reaction in comparison with the speed of the oxidation of formaldehyde by the same reagent.

Battelli (4) found that in the presence of liver and muscle extracts, formic acid was oxidized directly to carbonic acid. He assumed that the enzymes in these extracts catalytically aided in the oxidation.

Dakin, (5) while studying the catalytic effect of ammonia upon hydrogen peroxide oxidations in general, found

that the ammonium salt of formic acid was readily oxidized to carbonate by 3% hydrogen peroxide at room temperature.

More recently, Holden and Hatcher (6) studied the action of hydrogen peroxide upon formic acid with a view to determining the reaction rate. Their findings indicate the oxidation of formic acid to carbonic acid by a monomolecular reaction in which some performic acid is produced.

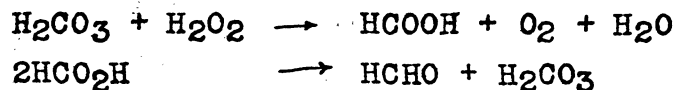
All of these references point to the fact that the oxidation in acid solution results in the production of carbonic acid alone, although the quantitative nature of the completed reaction was not definitely established. In no instance was an attempt made to correlate the amount of hydrogen peroxide used with the yield of carbonic acid produced, through which procedure alone could the reaction be quantitatively affirmed. In this connection the results of Wislicenus (7) are extremely interesting. This investigator stated that hydrogen peroxide in dilute solution acted as a reducing agent to bring about the production of formic acid from carbonic acid, a reaction which is quite the reverse of the expected oxidation. The equation for this reaction is as follows:



Wislicenus explains the reaction as involving the mutual disoxidation of two peroxides (carbonic acid being the only carboxylic acid besides per-acids in which the anions are of a peroxide nature) and hence no expenditure of energy

should take place. Thus hydrogen peroxide might in the same reaction mixture function both as an oxidizing agent and as a reducing agent, a fact which has been definitely established in other cases.

The results of Wislicenus have been verified recently by Rupp and Schlee (8) who found that in the presence of iron salts, sodium bicarbonate reacts with hydrogen peroxide producing formic acid, formaldehyde, carbon dioxide, and oxygen. These investigators postulate the following reactions to account for these products:

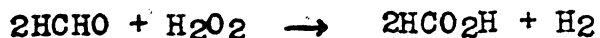


The concentrations of hydrogen peroxide used both by Wislicenus, and Rupp and Schlee, were very low, this probably accounting for the fact that the formic acid and formaldehyde were not oxidized back to carbonic acid. It will be noted that subsequent results obtained in this study confirm the fact that hydrogen peroxide in dilute solutions functions as a reducing agent.

The literature thus indicates that formic acid is oxidized directly to carbonic acid by hydrogen peroxide but that under some conditions a reverse reaction may take place resulting in the production of formic acid by the reducing action of hydrogen peroxide upon carbonic acid.

B. Formaldehyde

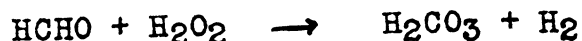
Although in basic solution the reaction,



has been definitely established by numerous investigators and is used as a quantitative method for the determination of formaldehyde, the reaction occurring in acid media is the subject of much discussion in the literature.

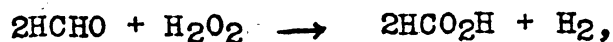
Kastle and Loevenhart (2) studied the reaction from the point of view of reaction rate and record that formaldehyde is oxidized quite readily to formic acid at 100°C., the reaction being accelerated by inorganic acids. No mention is made of the liberation of hydrogen so it is evident that these authors did not realize the true character of the reaction. Later the same authors (3) studied the relation between the rate of decomposition and the oxidative power of hydrogen peroxide upon formaldehyde, but again no mention is made of the liberation of hydrogen.

Geisow, (9) in direct contradiction to the above report of Kastle and Loevenhart, was unable to isolate any formic acid resulting from the oxidation of formaldehyde by hydrogen peroxide in either acid or neutral solution, and even at low temperatures. Hence he assumed that the formaldehyde was oxidized directly to carbonic acid with the liberation of hydrogen according to the following equation:

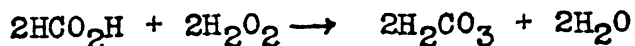


With concentrations of hydrogen peroxide of 3% and 30% the same results were obtained.

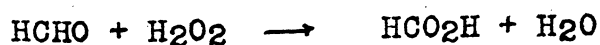
Again it is surprising to find that the work of Geisow is strongly refuted by Lyford (10) who states that formic acid is always produced as an intermediate product, along with hydrogen, in the oxidation of formaldehyde by hydrogen peroxide. Some of the formic acid may then be further oxidized to carbonic acid but except for prolonged action the reaction goes no farther than the intermediate stage. The principle reaction, according to Lyford, is



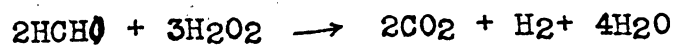
which is followed by the further oxidation of formic acid to carbonic acid:



Since the yield of hydrogen did not correspond to the theoretical amount from the Geisow equation, Lyford postulates that some of the hydrogen must be oxidized to water by the oxygen which is constantly evolved from the decomposition of hydrogen peroxide. In addition, he states that there seems to be a direct oxidation reaction,



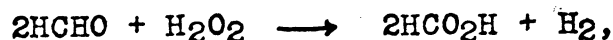
The first two above equations are then combined by Lyford into an empirical one demanding at least twice as much carbon dioxide as hydrogen.



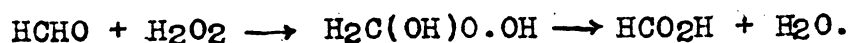
The results he obtained, however, do not verify this equation.

Cervello and Pitini, (11) working chiefly from the biological standpoint, verify the results obtained by Geisow. They state that, in the presence of animal extracts, formaldehyde is oxidized directly to carbonic acid with no intermediate production of formic acid.

More recently Bach and Generosov (12) studied the reaction at 70°C. and record that the reaction is incomplete at this temperature in the absence of alkali when the molecular ratio of formaldehyde to hydrogen peroxide is 2:1. The reason given for the incompleteness is that the free formic acid produced retards the reaction. When an excess of hydrogen peroxide was used it was found that the ratio of formic acid to hydrogen produced was not 2:1 as required by the following equation,



but was about 2.59:1. The authors postulate, therefore, that the reaction where an excess of hydrogen peroxide is present proceeds partly according to the above equation and partly by the following:

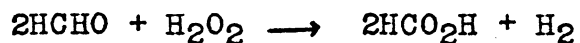


No mention is made of further oxidation to carbonic acid.

Wieland and Wingler (13) investigated only a complex formed between formaldehyde and hydrogen peroxide in dilute solutions.

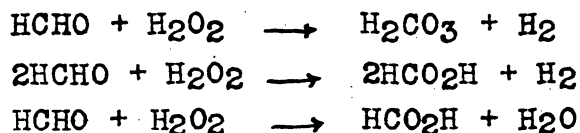
Hatcher and Holden (14) found that the reaction between hydrogen peroxide and formaldehyde at 25°C. and in

dilute solutions corresponded to the following equation,



Fifty-five percent conversion of formaldehyde to formic acid was obtained and the authors state that under the conditions of the experiments, no oxidation of formic acid to carbonic would occur.

It is at once evident from the above survey of the literature that no definite conclusions can be drawn as to the exact quantitative nature of the reaction between formaldehyde and hydrogen peroxide in acid solutions. The following reactions in summary have been postulated but the extent of each has not yet been definitely determined:



This situation calls for further quantitative investigation.

C. Methyl Alcohol

The action of hydrogen peroxide upon methyl alcohol has been the subject of very little study and no attempts have been made to explain the mechanism of the reaction.

Renard (15) in 1879, while studying the electrolytic oxidation of alcohols, attempted the oxidation of methyl alcohol with hydrogen peroxide, in an effort to determine whether the electrolytic oxidations were comparable with, and due to, the intermediate formation of hydrogen peroxide at the anode. Using various concentrations of hydrogen peroxide up to 10.3 volume in dilute sulphuric acid solutions he found that in no case was the methyl alcohol attacked, even after long standing. Renard thus concluded that hydrogen peroxide was without action on methyl alcohol.

Blank and Finkenbeiner (16) conducted oxidations of formaldehyde by hydrogen peroxide in methyl alcohol solutions, stating that the methyl alcohol is not attacked by hydrogen peroxide at low temperatures.

An apparently contradictory conclusion as to the action of hydrogen peroxide on methyl alcohol is found in the work of Frankforter and West, (17) who state that methyl alcohol is slowly oxidized to formic acid by hydrogen peroxide without the liberation of hydrogen, but give no data concerning this fact. The concentration of the hydrogen peroxide, and the temperature under which the

reactions were conducted are also not stated.

Heimrod and Levene (18) studied the action of hydrogen peroxide on methyl alcohol in basic solution and report that the methyl alcohol is slightly oxidized to formic acid at room temperatures by 30% peroxide solution. The reaction, according to Heimrod and Levene, apparently oversteps the intermediate formaldehyde state, as in no case could the presence of formaldehyde be detected. They further state that in no case was hydrogen given off, which is in agreement with the findings of Frankforter and West. Here again no quantitative data concerning the nature of the oxidation is given.

Schmiedel (19) recommends the oxidation of methyl alcohol to formic acid by hydrogen peroxide as a quantitative method for the determination of methyl alcohol in small quantities. In the procedure he cools the alkaline methyl alcohol solution to 50°C. "so that no oxidation to carbon dioxide will take place." Successive portions of dilute hydrogen peroxide solution are added and the yield of formic acid produced is determined by the reduction of mercuric chloride. The data obtained indicate a quantitative relationship between the initial amounts of methyl alcohol used and the yields of formic acid obtained, but only when very small amounts of methyl alcohol are present.

Doroshevskii and Bardt (20) found that methyl alcohol is oxidized to a mixture of formaldehyde and formic

acid by the action of hydrogen peroxide in the presence of manganous or ferrous salts. Again no data were obtainable concerning the percent oxidation taking place, or concerning the conditions imposed, other than the presence of a catalyst.

It is apparent from this review of the literature pertaining to methyl alcohol that very little work of a quantitative nature has been done on the problem of its action with hydrogen peroxide, and that no definite conclusions can be drawn as to whether any reaction takes place, what products are formed, or under what conditions, if the two compounds react.

D. Acetic Acid

Passing from compounds containing one carbon atom to corresponding compounds containing two carbon atoms, most of the investigations concerning the action of hydrogen peroxide upon acetic acid are related to the intermediate formation of acetic acid in the oxidation of some higher organic compound by hydrogen peroxide. This fact makes a search of the literature on the subject not only difficult but subject to possible unavoidable error. The following references undoubtedly cover the principle literature relating to the reaction, as obtainable from not only a perusal of the literature pertaining directly to acetic acid, but also to higher compounds, such as ethyl alcohol, acetaldehyde, butyric acid, and the like, which are likely to yield acetic acid upon oxidation. Those references indicating that acetic acid is not attacked by hydrogen peroxide are omitted owing to their vagueness and apparent lack of importance.

Dakin (21) records that acetic acid, formed intermediately in the oxidation of butyric acid by hydrogen peroxide, is further oxidized to formic acid, carbon dioxide, and water. The work is chiefly qualitative but indicates the following reaction at 37°C.



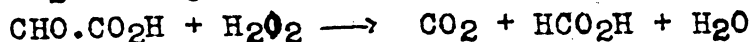
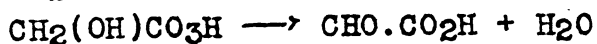
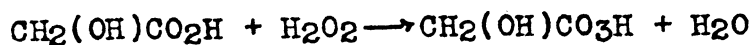
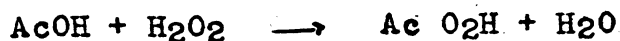
Heimrod and Levine (18) state that acetic acid, formed intermediately in the oxidation of acetaldehyde by

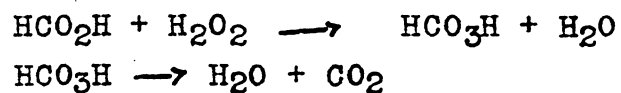
hydrogen peroxide in alkaline solutions at 0°C. is oxidized further to formic acid, carbon dioxide, and water, apparently by the reaction given in the preceding reference.

Knoop and Gehrke, (22) in considering biological oxidations, found that acetic acid subject to the action of dilute hydrogen peroxide solutions for several weeks, apparently at body temperature, suffered only 2% to 4% oxidation. The products of oxidation are not given.

Walton and Christiansen (23) obtained acetic acid upon oxidizing ethyl alcohol with hydrogen peroxide in the presence of iron salts. The acetic acid is then further oxidized to carbon dioxide and water. No mention is made of the presence of formic acid.

Perhaps the best work on the reaction between acetic acid and hydrogen peroxide has been done by Hatcher and Holden (14). They treated acetic acid with 10% hydrogen peroxide at 100°C. and found 5.5% oxidation took place in one hour, with production of formic acid as an intermediate product. The following reactions giving the intermediate formation of glycolic, glyoxylic, and formic acids, together with peracetic, perglycolic, and performic acid are postulated as possible mechanisms.





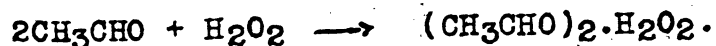
The literature thus indicates that acetic acid is oxidized quite slowly to carbonic acid, with the intermediate production of formic acid. Here also the lack of quantitative study of the reaction again calls for further investigation.

E. Acetaldehyde

Attempts to apply reactions analogous to those of formaldehyde and hydrogen peroxide to the next member of the homologous series, acetaldehyde, have failed in basic solution owing to the fact that acetaldehyde condenses to a resin in the presence of strong alkalis, and polymerizes to aldols in dilute alkalis. In acid and neutral media, however, acetaldehyde has been found to be oxidized, and in only one instance has hydrogen been reported as one of the products of the reaction.

Blank and Finkenbeiner (16) obtained some hydrogen by the action of hydrogen peroxide on acetaldehyde in dilute basic solutions. No quantitative data on the reaction is given and the investigators question the quantitative nature of the reaction.

Baeyer and Villiger, (24) interested chiefly in oxonium compound formation, give evidence to the fact that acetaldehyde forms a diacetaldehyde peroxide hydrate with hydrogen peroxide at room temperature as follows:



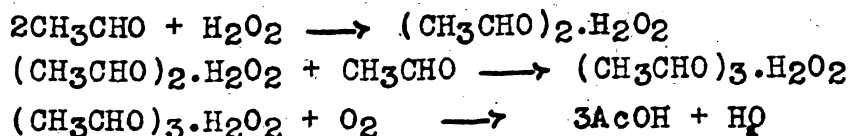
Geisow (9) attempted to carry the analogy of the liberation of hydrogen by the action of hydrogen peroxide upon formaldehyde in basic solution, to the liberation of methane from acetaldehyde under similar conditions. He was unable to obtain any methane and accordingly concluded that the oxidation of acetaldehyde was a different type of

reaction. It should here be noted parenthetically as pertinent to subsequently described experiments of the research that not only hydrogen but also methane are products of the oxidation of acetaldehyde by hydrogen peroxide in acid media. This discovery has, as will be shown later, a most important bearing upon the interpretation of the mechanism of the reaction.

Dakin (21) found acetaldehyde as one of the intermediate products formed in the oxidation of butyric acid by hydrogen peroxide. Since formic acid, acetic acid, and carbonic acid are further oxidation products he assumed that acetaldehyde is oxidized to these acids. No mention of hydrogen liberation is made.

Heimrod and Levene (18) record that acetaldehyde in alkaline solution of hydrogen peroxide is oxidized with the formation of acetic acid, formic acid, and carbon dioxide, at 0°C. They further state that no formaldehyde is produced by the reaction.

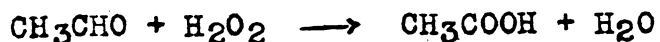
Reiner (25) verified the compound formation as noted by Baeyer and Villiger and in addition postulated further reactions according to the equations:



Thus the triacetaldehyde peroxide hydrate is oxidized by free oxygen directly to acetic acid.

Hatcher and Toole (26) found the reaction between

hydrogen peroxide and acetaldehyde at low temperature to be monomolecular, corresponding to the direct oxidation of the aldehyde to acetic acid according to the equation,



At high temperature the acetic acid is further attacked by the hydrogen peroxide and glycolic, glyoxylic, formic, and carbonic acids are the products as noted in Part D relating to acetic acid. Again no mention is made of the liberation of hydrogen or methane.

The fact that in only one case has the liberation of hydrogen and in no case the liberation of methane by the action of hydrogen peroxide on acetaldehyde been recorded, clearly shows that the reaction is worthy of further quantitative study, and as noted above, will have a direct bearing upon the interpretation of the reaction mechanism.

THEORY AND OBJECT OF THE INVESTIGATION

The primary objects in undertaking this investigation were:

(1) To determine both qualitatively and quantitatively the several products of oxidation resulting from the action of hydrogen peroxide upon: (A) Formic acid; (B) Formaldehyde; (C) Methyl alcohol; (D) Acetic acid; (E) Acetaldehyde.

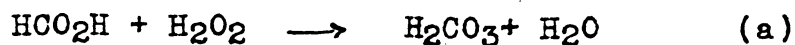
(2) To ascertain the quantitative extent to which each of the reactions postulated to explain the oxidation products, occurs.

(3) From the results obtained in (1) and (2), to formulate a mechanism to explain the action of hydrogen peroxide upon the compounds investigated.

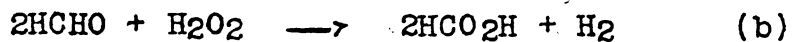
Since the oxidation of simple carbon compounds is the subject of investigation, and since the alcohols are the simplest type of carbon compounds readily susceptible to oxidation, the action of hydrogen peroxide upon methyl alcohol would naturally be the first reaction to be studied. But since the methyl alcohol may yield on oxidation successively, formaldehyde, formic acid, and carbonic acid, it was deemed more advisable to investigate first the action of hydrogen peroxide upon formic acid, then upon formaldehyde, and finally upon methyl alcohol.

A. Formic Acid

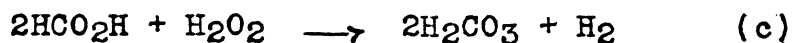
Since formic acid is quite readily oxidized by comparatively weak oxidizing agents such as mercuric chloride, to carbonic acid, it would seem that the reaction with hydrogen peroxide should be a simple oxidation as follows:



However, formic acid contains an aldehyde grouping which, in addition to accounting for its ease of oxidation might make it susceptible to another parallel reaction, namely, the liberation of hydrogen as is shown by formaldehyde according to the following equation given in Part II.



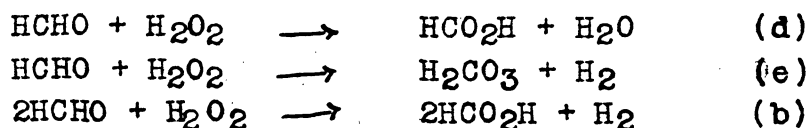
The corresponding reaction for formic acid would be



It will be shown in Part IV, however, that no hydrogen is obtained according to reaction (c).

B. Formaldehyde

For the action of hydrogen peroxide upon formaldehyde the following reactions are possible and all of them have been postulated, as noted in Part II, singly and in various combinations by various investigators, to explain the reaction mechanism:



In addition, reaction (a) for the oxidation of formic to carbonic acid by hydrogen peroxide may take place.

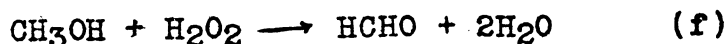
With formaldehyde the expected normal oxidation to formic acid (equation d) and thence to carbonic acid (equation a) is complicated by the seemingly paradoxical liberation of hydrogen (Equation e). It would be expected that with a relatively strong oxidizing agent such as hydrogen peroxide, any labile hydrogen would be oxidized to water quite readily. The liberation of hydrogen would seem therefore to indicate simultaneous oxidation-reduction reaction, thereby proving that the hydrogen peroxide functions both as an oxidizing and a reducing agent. This property of hydrogen peroxide has a vital bearing upon the subsequently proposed mechanism of reaction. That hydrogen peroxide may function as a reducing agent has already been noted in (A) of Part II, where hydrogen peroxide has been shown to bring about the production of formic acid from

carbonic acid. This apparently anomalous fact also calls for an explanation in terms of the proposed reaction mechanism.

Since reaction (b) has been shown conclusively to be the only reaction occurring in basic media, it would seem that this reaction should also explain the liberation of hydrogen in acid media. However, it is noted in the literature that in no case was an equivalent amount of hydrogen liberated corresponding to this reaction, and in several instances the production of carbonic acid is recorded. This would indicate the concurrence of reactions (a) and (b) and possibly also reactions (d) and (e). It will be shown in the Experimental Part IV that (b) and (d) are concurrent reactions, being followed by reaction (a).

C. Methyl Alcohol

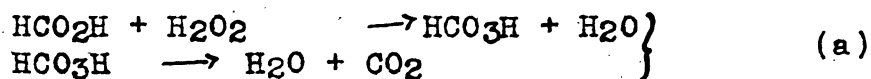
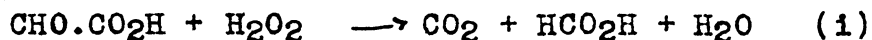
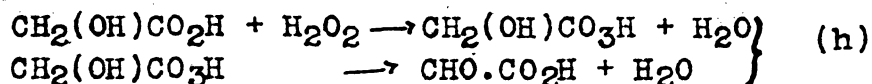
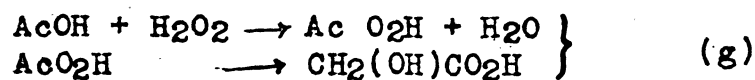
From a theoretical standpoint, the oxidation of methyl alcohol by hydrogen peroxide should proceed through the successive formaldehyde and formic acid intermediate stages and give carbonic acid and water as final products. If this mechanism is correct, therefore, the reaction should be accompanied by the liberation of hydrogen from the action of hydrogen peroxide on the intermediately produced formaldehyde. Thus in addition to the reactions already proposed for formic acid and formaldehyde, it would only be necessary to postulate the first reaction, namely, the production of formaldehyde by the first step in the oxidation of methyl alcohol as follows:



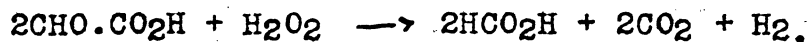
Since the liberation of hydrogen from methyl alcohol has not been previously recorded, the results given in Part IV offer the first definite proof of the concurrence of the reactions noted above.

D. Acetic Acid

The unexpected results of the action of hydrogen peroxide upon formaldehyde and methyl alcohol virtually led to an extension of the study to higher members of the corresponding homologous series. The question as to whether acetaldehyde and ethyl alcohol undergo similar reactions necessitated first a study of the action occurring between hydrogen peroxide and acetic acid. The mechanism of the oxidation of acetic acid by hydrogen peroxide as proposed by Hatcher and Holden (14) seems quite acceptable. They propose the following steps as given in Part II.



The isolation of glycolic and glyoxylic acids from this reaction have never been accomplished so their actual presence is doubtful. Formic acid, however, has been definitely proven to be present. If glyoxylic acid is an intermediate compound, and if aldehydes in general liberate hydrogen in the presence of hydrogen peroxide, the reaction also may result in the production of hydrogen according to the equation



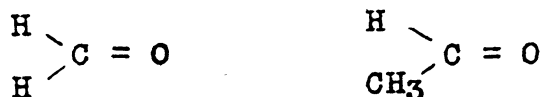
which is quite parallel to the formaldehyde reaction (b).



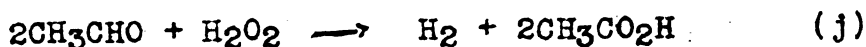
Since no hydrogen was found in the reaction with acetic acid as will be shown in Part IV and since hydrogen is found to be liberated from acetaldehyde under the same conditions, it seems probable that no glyoxylic acid is formed. Conclusive evidence from a direct study of glyoxylic acid alone, however, has not been obtained.

E. Acetaldehyde

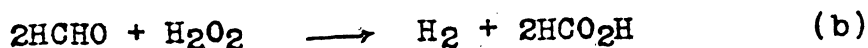
Acetaldehyde may be considered to be derived from formaldehyde by the substitution of a methyl group for one hydrogen atom as follows:



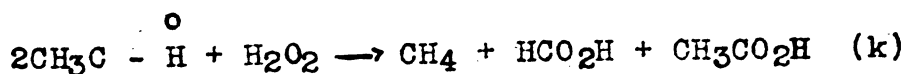
Hence acetaldehyde would react with hydrogen peroxide in conformity with the equation (j),



which is parallel to the formaldehyde equation (b)

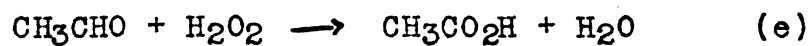


There is only one reference in the literature (16)
to the occurrence of reaction (j). It is also conceivable that methane may be liberated when hydrogen peroxide reacts with acetaldehyde according to the assumed equation (k), thus



There is no notation in the literature of the occurrence of this reaction. This assumption has been verified in the Experimental Part IV and the established fact that not only hydrogen, but also methane is evolved has an important bearing upon the subsequently proposed reaction mechanism.

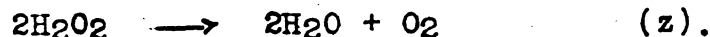
In addition to reactions (j) and (k) the normal oxidation of acetaldehyde to acetic acid according to equation (e) should likewise take place.



It will be shown subsequently that this latter reaction predominates.

EXPERIMENTAL

In practically all of the previous investigations recorded in the literature involving the use of hydrogen peroxide as an oxidizing agent, no attempt has been made to correlate quantitatively the extent of oxidation, with the amount of hydrogen peroxide consumed. Knowing the initial quantity of hydrogen peroxide present in a given reaction mixture, and determining the yields of the products of oxidation, it is possible to determine the total quantity of hydrogen peroxide entering into reaction. This total quantity of hydrogen peroxide reacting is the sum of several fractions of hydrogen peroxide, each fraction functioning to a greater or lesser extent in a corresponding reaction, in conformity with one or more equations. Of course, a certain fraction of the initial quantity of hydrogen peroxide undergoes direct decomposition into water and molecular oxygen according to the well-known equation



The hydrogen peroxide equivalent to this oxygen, when subtracted from the initial quantity of the hydrogen peroxide gives the total quantity which reacts with the carbon compounds present in the reaction mixture. In most instances it was thus possible to calculate the quantity of these separate fractions of the hydrogen peroxide which effected the one or more postulated reactions.

Accordingly, experimental methods of procedure

were devised to ascertain the quantitative yields of each of the possible products of reaction, and the fractions of the quantities of hydrogen peroxide utilized in effecting the several reactions postulated.

Throughout the investigation, the hydrogen peroxide used was the so-called "one hundred volume", containing thirty percent by weight of hydrogen peroxide. This was obtained free from preservatives of an organic nature and contained a small amount of sulphuric acid together with a trace of phosphoric acid as prepared by the Roessler-Hasslacher Chemical Company, Niagara Falls, New York, and kindly donated by their president, Dr. H. R. Carveth. The total acidity of the peroxide was determined by titration, using methyl orange as indicator, after decomposing a given amount of the peroxide by boiling with silica.

The initial quantity of hydrogen peroxide used in each reaction mixture was determined by titration of the hydrogen peroxide solution with potassium permanganate according to the standard method (1). It was found that the hydrogen peroxide must be titrated immediately before use due to the appreciable decomposition of the peroxide at room temperatures. When not in use the peroxide remained quite stable when cooled below 40°F. The amount of the hydrogen peroxide decomposing according to equation (2) during the course of the reaction was measured

gasometrically from the volume of oxygen evolved. From the difference between the amount of hydrogen peroxide originally used and the amount equivalent to the oxygen evolved, the hydrogen peroxide actually used in the oxidation reaction would be evident. This will be referred to subsequently as the active hydrogen peroxide.

A. Formic Acid

1. Procedure

The apparatus consisted of a 250 cc. Pyrex reaction flask connected through a 30 cm. upright Liebig condenser to calcium chloride drying tubes and thence to a carbon dioxide absorption U-tube of 28 cm. length arms filled with granular soda lime. The carbon dioxide absorption tube was connected in turn to another calcium chloride safety tube and then to a gas collecting bottle, where the gases evolved in the reaction could be collected over water.

Through the top of the condenser a tube with a stopcock led into the reaction flask so that a stream of nitrogen could be passed into the apparatus and displace all air before the reaction was started. All connections were glass sealed with the exception of those between the reaction flask and the condenser, and the two joining the carbon dioxide absorption tube to the apparatus. These were sealed with extra hard DeKhotinsky cement which formed a perfectly gas tight joint but still allowed the easy removal of these parts from the remainder of the apparatus. No rubber tubing or rubber stoppers were permissible since both were found to be quite permeable to gases, especially hydrogen.

Kahlbaum's pure formic acid was redistilled and the portion of constant boiling point 100.5°C . was selected for use in the following experiments. The apparatus described

above was set up in duplicate, care being taken in the selection of flasks of uniform structure and smooth internal surfaces to prevent as far as possible decomposition of hydrogen peroxide, which is catalyzed by rough surfaces. The condensers were of the same size and a uniform stream of water was circulated through them. One fourth of a mole of formic acid (11.5 grams) was carefully weighed into each of the reaction flasks, then one fourth of a mole of hydrogen peroxide was added from a calibrated burette. Enough sulphuric acid was then introduced into each flask to make the total amount, including that initially present in the hydrogen peroxide, equal 2.16 grams. Distilled water was added finally, making the total volume of this reaction mixture equal 125 cc. The flasks were connected to the upright condensers and sealed with DeKhotinsky cement, both flasks were immersed in the same constant-level water bath. All air was then swept out of the apparatus by a stream of nitrogen. The water bath was then heated to boiling.

After heating for five hours, the reaction appeared to be complete as no more gas was evolved. Five grams of finely divided silica were then added through the nitrogen delivery tube and gently blowed into the reaction flask by means of a stream of nitrogen. In this manner no gas was allowed to escape from the apparatus. The silica brought about the decomposition of any remaining hydrogen peroxide in the reaction flask through the catalytic action of the large

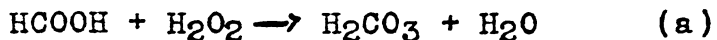
surface presented. After remaining in the presence of the silica for two hours (which time has been shown previously to completely decompose all peroxide), (1) the gas in the apparatus was slowly displaced into the gasometer by means of nitrogen. It was necessary to pass the nitrogen through slowly due to the great amount of carbon dioxide remaining in the flask and condenser. The passage of nitrogen was continued until the tubes had cooled and ample time had been allowed for sweeping all the gas into the gasometer.

The contents of the reaction flasks were transferred to volumetric flasks and then diluted to 250 cc. Ten cc. aliquot portions were titrated with standard alkali, using phenolphthalein as an indicator. Subtraction of the acidity corresponding to the sulphuric acid present from the total acidity thus found in each case, gave the amount of formic acid remaining at the completion of the reaction.

The yield of carbon dioxide, as determined from the increase in weight of the soda-lime tubes, indicated the extent of the oxidation of the formic acid to carbonic acid.

Having determined the formic acid remaining unattacked, and that oxidized to carbonic acid, the gas collected during the reaction was analyzed for possible gaseous products of the reaction. No hydrogen or carbon monoxide were found to be present, indicating that the sole reaction between formic acid and hydrogen peroxide is a direct oxidation of the formic acid to carbonic acid

according to equation (a) proposed in Part III.



If this is correct the yield of carbonic acid should correspond mole for mole to the amount of hydrogen peroxide effecting the oxidation, that is, the active hydrogen peroxide. The amount of hydrogen peroxide decomposing into molecular oxygen and water during the reaction was then determined from a measure of the oxygen collected in each case. The percentage of oxygen in the gas was ascertained by use of the standard Hempel gas analysis apparatus, the oxygen being absorbed over phosphorous. From the contraction in volume, the percentage of oxygen and hence the total volume collected was readily obtained. This volume was reduced to standard conditions of temperature and pressure, and its hydrogen peroxide equivalent calculated. Deducting this amount of hydrogen peroxide from the initial quantity of hydrogen peroxide used, gave the amount of active hydrogen peroxide.

2. Data

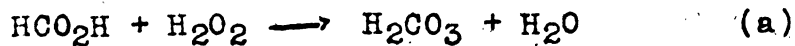
Table I gives the data obtained from the duplicate runs conducted according to the above procedure.

TABLE I

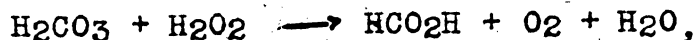
Run	Formic Acid						
	I	II	III	IV	V	VI	VII
	Initial H ₂ O ₂ Moles	Initial HCO ₂ H Moles	H ₂ CO ₃ found Moles	% oxidation HCO ₂ H → H ₂ CO ₃	H ₂ O ₂ ⇌ H ₂ CO ₃ (Equa. a) Moles	H ₂ O ₂ ⇌ O ₂ (Equa. z) Moles	Total H ₂ O ₂ Eq. (a) + (z)
a	.2500	.2500	.1896	76.20	.1896	.0670	.2565
b	.2500	.2500	.1883	76.36	.1883	.0666	.2549

3. Conclusions.

Since no hydrogen is liberated through the action of hydrogen peroxide upon formic acid and since carbonic acid is the only oxidation product formed, it is evident that the reaction can only be expressed by equation (a). This is verified by the fact that the hydrogen peroxide consumed in the oxidation checks, within the limit of experimental error, with the amount of hydrogen peroxide theoretically necessary to produce the yield of carbonic acid experimentally obtained. Thus the reaction is definitely proven to be as follows:



The question as to whether any reduction of the carbonic acid occurs according to the equation of Wislicenus,



could not be established by the experimental method employed. From results subsequently obtained, however, it will be shown that hydrogen peroxide functions as a reducing agent only in dilute solutions, so it is probable that under the above conditions the reduction of carbonic acid occurs to only a negligible extent.

The fact that formic acid is directly oxidized to carbonic acid serves to simplify the subsequent study of the action of hydrogen peroxide upon formaldehyde which yields formic acid as an intermediate product.

B. Formaldehyde

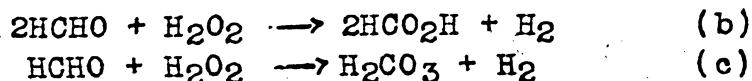
1. Procedure

Using the apparatus described in (A), the reaction between hydrogen peroxide and formaldehyde was investigated. Owing to the difficulty encountered in attempting to obtain formaldehyde solutions free from formic acid and methyl alcohol, the formaldehyde was used in the form of Merck's C.P. trioxymethylene. Since this polymer decomposes quantitatively into formaldehyde upon heating with dilute sulphuric acid solutions, this afforded not only an easy method of obtaining practically pure formaldehyde but of introducing into reaction mixtures definite quantities.

From preliminary runs, it was found that the reaction between formaldehyde and hydrogen peroxide was entirely too vigorous at 100°C. to permit the use of the described apparatus. At 60°C., however, the reaction was found to proceed smoothly and reach completion in approximately five hours. The reactions were consequently conducted at 60°C., the temperature being controlled by immersing the reaction flasks up to the neck, in a constant temperature thermostat. A series of duplicate runs was then conducted, using one fourth mole of formaldehyde in each case and varying the quantity of hydrogen peroxide successively to 1/16, 1/8, 1/4, 1/2, 3/4 and one mole in the reaction mixture of constant volume, 125 cc. The use of trioxymethylene made possible the direct weighing of

the formaldehyde into the reaction flasks. The hydrogen peroxide, and sulphuric acid to make 2.16 grams in each case, were added as previously described, and the volumes made up to 125 cc. with distilled water.

After five hours the reactions in every case were complete as shown by the cessation of the liberation of gases and also by the absence of hydrogen peroxide in determinable quantities, in the reaction flasks. The contents of the flasks were analyzed for formic acid by titration of increase in acidity in the manner described under Formic Acid (A). Carbonic acid was determined as before and the gas collected was analyzed for hydrogen, carbon monoxide and oxygen. In no case was carbon monoxide found to be present. Oxygen was determined as before, and hydrogen was determined by the pipette explosion method. The liberation of hydrogen indicates clearly the occurrence of either or both of the previously noted reactions (b) and (c) of Part III.



The formation of carbonic acid indicates the occurrence of reaction (c), just recorded or (a) noted above, or both (c) and (a).

2. Data.

The results obtained from the above series of runs are found in Tables IIA to VIIIA, inclusive, covering

respectively the runs involving $1/16$, $1/8$, $1/4$, $1/2$, $3/4$
and 1 mole of hydrogen peroxide with $1/4$ mole of formaldehyde.

TABLE II

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	.0625	.2500	.1184	.0000	.0563	.0002
b	.0625	.2500	.1185	.0000	.0565	.0002

B.

Run	1 % yield H ₂ ⇌ HCHO Eq. (b)	2 % yield HCO ₂ H ⇌ HCHO Eq. (d)	3 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used ⇌ H ₂ Eq. (b)	5 % H ₂ O ₂ used ⇌ HCO ₂ H Eq. (d)	6 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq. (a)	7 % H ₂ O ₂ used ⇌ O ₂ Eq. (z)	8 Total % H ₂ O ₂ used
a	95.10	4.90	0.00	90.08	9.28	0.00	0.64	100.00
b	95.36	4.64	0.00	90.40	8.80	0.00	0.64	99.84

TABLE III

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	.1250	.2500	.2250	.0011	.1048	.0013
b	.1250	.2500	.2256	.0010	.1043	.0011

B.

Run	1 % yield H ₂ & HCHO Eq. (b)	2 % yield HCO ₂ H & HCHO Eq. (d)	3 % yield H ₂ CO ₃ & HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used & H ₂ Eq. (b)	5 % H ₂ O ₂ used & HCO ₂ H Eq. (d)	6 % H ₂ O ₂ used & H ₂ CO ₃ Eq. (a)	7 % H ₂ O ₂ used & O ₂ Eq. (z)	8 Total % H ₂ O ₂ used
a	92.70	7.30	0.48	83.84	13.20	0.88	2.08	100.00
b	92.06	7.94	0.48	83.44	14.40	0.80	1.76	100.40

TABLE IV

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	.2500	.2500	.1911	.0597	.0854	.0091
b	.2500	.2500	.1920	.0597	.0863	.0086

B.

Run	1 % yield H ₂ ⇌ HCHO Eq.(b)	2 % yield HCO ₂ H ⇌ HCHO Eq. (d)	3 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used ⇌ H ₂ Eq.(b)	5 % H ₂ O ₂ used ⇌ HCO ₂ H Eq.(d)	6 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq.(a)	7 % H ₂ O ₂ used ⇌ O ₂ Eq.(z)	8 Total % H ₂ O ₂ used
a	68.10	31.90	23.81	34.16	32.00	23.88	7.28	97.32
b	68.57	31.43	23.72	34.52	31.64	23.88	6.88	96.92

TABLE V

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	.5000	.2500	.0863	.1674	.0458	.0585
b	.5000	.2500	.0861	.1679	.0455	.0580

B.

Run	1 % yield H ₂ ← HCHO Eq. (b)	2 % yield HCO ₂ H → HCHO Eq. (d)	3 % yield H ₂ CO ₃ → HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used → H ₂ Eq. (b)	5 % H ₂ O ₂ used → HCO ₂ H Eq. (d)	6 % H ₂ O ₂ used → H ₂ CO ₃ Eq. (a)	7 % H ₂ O ₂ used → O ₂ Eq. (z)	8 Total % H ₂ O ₂ used
a	36.11	63.89	65.98	9.16	32.42	33.48	23.40	98.46
b	35.83	64.17	66.10	9.10	32.68	33.58	23.20	98.48

TABLE VI

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	.7500	.2500	.0335	.2214	.0308	.1472
b	.7500	.2500	.0327	.2230	.0307	.1460

B.

Run	1 % yield H ₂ ⇌ HCHO Eq. (b)	2 % yield HCO ₂ H ⇌ HCHO Eq. (d)	3 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used ⇌ H ₂ Eq. (b)	5 % H ₂ O ₂ used ⇌ HCO ₂ H Eq. (d)	6 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq. (a)	7 % H ₂ O ₂ used ⇌ O ₂ Eq. (z)	8 Total % H ₂ O ₂ used
a	24.17	75.83	86.86	4.11	25.79	29.52	39.25	98.67
b	24.01	75.99	87.21	4.10	24.91	29.73	38.93	98.67

TABLE VII

Formaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial HCHO moles	3 HCO ₂ H found moles	4 H ₂ CO ₃ found moles	5 H ₂ found moles	6 O ₂ found moles
a	1.0000	.2500	.0107	.2317	.0226	.2612
b	1.0000	.2500	.0117	.2326	.0227	.2596

B.

Run	1 % yield H ₂	2 % yield HCO ₂ H ↔ HCHO Eq.(d)	3 % yield H ₂ CO ₃ ↔ HCO ₂ H Eq. (a)	4 % H ₂ O ₂ used ↔ H ₂ Eq.(b)	5 % H ₂ O ₂ used ↔ HCO ₂ H Eq. (d)	6 % H ₂ O ₂ used ↔ H ₂ CO ₃ Eq.(a)	7 % H ₂ O ₂ used ↔ O ₂ Eq.(z)	8 Total % H ₂ O ₂ used
a	18.64	81.36	95.59	2.26	19.72	23.17	52.24	97.39
b	18.59	81.41	95.21	2.27	19.90	23.26	51.92	97.35

SUMMARY TABLE VIII

Formaldehyde

Run	Moles H_2O_2	Per cent by Reaction (b)	Per cent by Reaction (d)	Per cent by Reaction (g)
II	1/16	95.23	4.77	0.00
III	1/8	92.38	7.62	0.46
IV	1/4	68.33	31.67	23.76
V	1/2	35.97	64.03	66.04
VI	3/4	24.09	75.91	87.04
VII	1	18.62	81.38	95.40

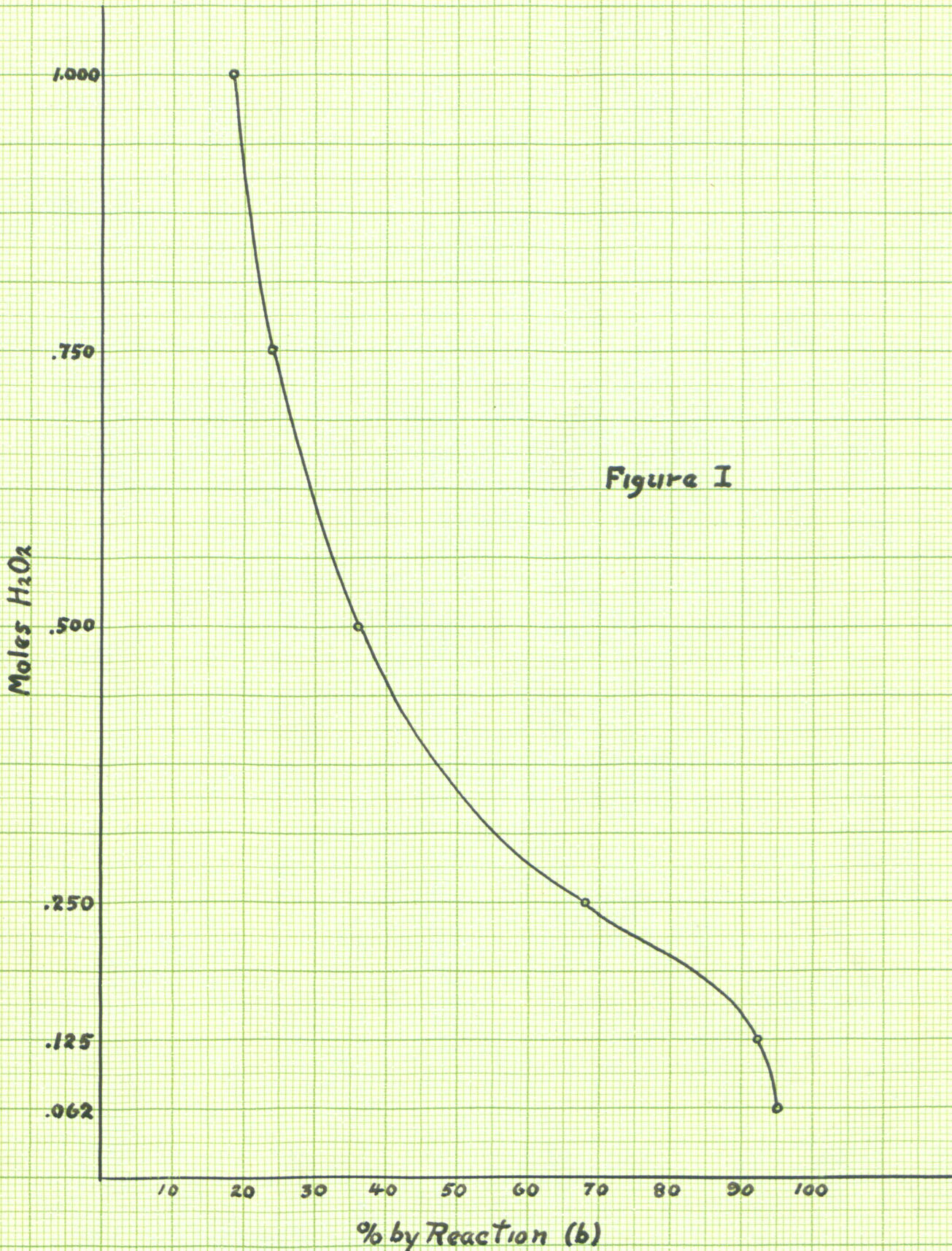
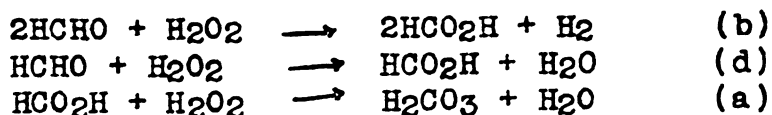


Figure I

In the above and following tables, the data of Part A of each table records the molar yields of the several products while the data of Part B gives the percentage yields of the products calculated from the several equations for the proposed reactions, thus facilitating comparison of the extents of occurrence of the concurrent reactions as effected by various concentrations of hydrogen peroxide. The amounts of hydrogen peroxide reacting according to the various equations are separately recorded and are also totaled in order to account for the total quantity of hydrogen peroxide in each of the duplicate sets of runs.

3. Conclusions

It is noted in Table IIA that hydrogen is liberated from formaldehyde without the production of carbonic acid, and since no hydrogen is produced by the oxidation of formic acid to carbonic acid as shown in Experimental Part IV A, the following equations, noted separately in Part III, represent the possible reactions occurring along with the decomposition of hydrogen peroxide into molecular oxygen and water.



Formic acid may be produced by either reaction (b) or (d), or both. If reaction (a) is the only one occurring, there should be formed one mole of hydrogen for every two

moles of formic acid. Furthermore, only one mole of hydrogen peroxide should be required for the completed reaction. From the Tables IIA to VIIA it is evident, however, that in no case was this ratio found to exist. In all instances the ratio of formic acid to hydrogen is seen to be greater than two to one, indicating that reaction (d) must also be taking place. Assuming that reactions (b) and (d) proceed simultaneously, the extent of the occurrence of reaction (b) may be directly calculated from the yield of hydrogen, and hence the quantity of formic acid equivalent to this yield of hydrogen, when subtracted from the total yield of formic acid, gives the quantity of formic acid produced according to equation (d) and thus indicates the extent of the occurrence of reaction (d). The amount of formic acid undergoing further oxidation to carbonic acid, according to equation (a), is obtained directly from the yield of carbon dioxide.

Tables IIB to VIIB record the extent of the occurrence of reactions (b), (d), and (a) in columns 1, 2, and 3 respectively. The last column, 8, in each case indicates the total percentage of the initial amount of hydrogen peroxide used in the reaction mixture, (a part of which effects oxidation according to (b), (d), and (a), while the remainder suffers simple decomposition into oxygen and water) accounted for on the basis of these reactions from the yield of oxidation products obtained.

The data given in Column 8, Tables IIB to VIIB are significant in that they give a check both on the type of reactions occurring, and also on the accuracy of the experimental method. It will be noted that within the limits of experimental error, these values agree well, practically 100 percent, with the initial quantities of hydrogen peroxide used. This is direct evidence of the fact that the reactions postulated are occurring to the extent calculated from the oxidation products.

Regardless of the concentration of hydrogen peroxide used, the results given in Tables II to VII show conclusively that reactions (b) and (d) are always concurrent. The data in Tables II-IV moreover, show that reaction (b) predominates when the molar ratio of hydrogen peroxide to formaldehyde is less than two to one. Thus from Table II, where the molar ratio of hydrogen peroxide to formaldehyde is one to four, it is seen that over 95% of the formic acid results from reaction (b), while with increasing concentrations, this reaction falls off steadily with a corresponding increase in reaction (d) until in Table VII, where the ratio is four to one, the former reaction (b) proceeds to only 18% while the latter reaction (d) has increased to 82%. Summary Table VIII brings out more clearly this relationship. This decrease of reaction (b) with increasing concentration of peroxide is shown by the graph, Figure 1, in which the percentage

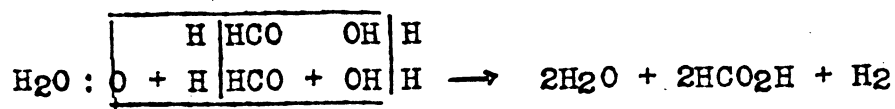
of the total reaction proceeding in this direction is plotted against the moles of hydrogen peroxide initially present. The curve apparently approaches asymptotically a limiting value of about 98% at zero concentration and 12% at infinite concentration of hydrogen peroxide, showing that the two reactions are always concurrent regardless of the concentration.

Concerning the secondary reaction (a), it will be noted from Table II that no oxidation of formic acid to carbonic acid occurs when the hydrogen peroxide-formaldehyde molar ratio is one to four. This reaction, however, does take place and increased with increasing amounts of hydrogen peroxide, as would be expected, until the results in Table VII show that over 95% of the formic acid is oxidized to carbonic acid.

The decomposition of hydrogen peroxide proceeds of course in all cases, naturally being much more extensive in the more concentrated solutions.

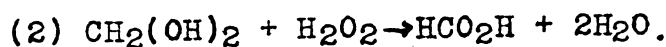
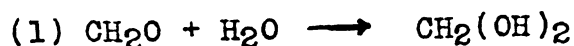
Reaction Mechanism of the Liberation of Hydrogen

Two possible mechanisms have been postulated to explain the liberation of hydrogen from formaldehyde by the action of hydrogen peroxide. Traube (27) considered that the methylene group in formaldehyde is not affected by hydrogen peroxide. The hydrogen, therefore, must come from the hydrogen peroxide or the water. Since, however, hydrogen free oxidizing agents such as potassium chromate, also set free hydrogen, the latter must come from the water. Traube's theory postulates that since no oxidation occurs in the absence of water, the reaction between the oxidizable substance and the oxidizing agent takes place so that the former takes an hydroxyl group and the latter a hydrogen atom, as follows:

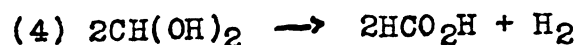
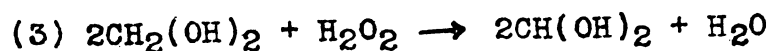


The rectangular enclosure is used to indicate the intermediate formation of a molecular complex which is formed with the liberation of hydrogen and is then followed by loss of water. That the H₂O₂ is not attacked by nascent hydrogen is explained by Traube as being due to the production of molecular hydrogen much more rapidly than the reduction by hydrogen of the formaldehyde-hydrogen peroxide complex can proceed. This theory seems to be supported by the observations of Legler, (28) that hexoxymethylene triperoxide (CH₂O)₆.03.3H₂O reacts with water to yield formic acid, water, and hydrogen.

Wieland (29) has proposed a theory in which formaldehyde is considered to react in the hydrated form. The direct oxidation of formaldehyde by hydrogen peroxide to formic acid and water would, therefore, be pictured in two steps:



To explain the production of hydrogen, part of the aldehyde hydrate must react with hydrogen peroxide to form a complex which then breaks down into formic acid and hydrogen:



Traube's theory, proposing the hydrogen as coming from the water, seems unlikely, for if such is the case there is no reason why hydrogen should not be produced from every oxidation reaction in the presence of water, regardless of the compound undergoing oxidation. It is quite generally conceded that the methylene group in formaldehyde is readily susceptible to oxidation and other reactions, and since this group is almost unique to formaldehyde, it would seem logical to account for the unusual reaction, whereby hydrogen is liberated from this compound, to the presence of such a structure.

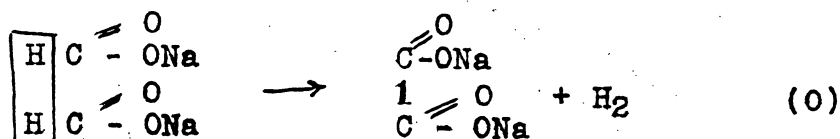
The dehydrogenation theory of Wieland seems more logical but in the interests of simplicity of explanation, it seems unnecessary to consider formaldehyde as reacting in the hydrated form.

Since both of the hydrogen atoms in formaldehyde are similar in position, it is possible that either one or both may be liberated by the action of hydrogen peroxide. Since the removal of two hydrogen atoms from one molecule of formaldehyde would result in the formation of carbon monoxide, and since carbon monoxide is not one of the products of the reaction, it is more likely that one atom of hydrogen must come from each of two molecules of formaldehyde, as would be indicated by Wieland's theory. If his mechanism is correct, however, there is no explanation of the fact, as shown in Table VIII, that with increasing peroxide concentrations, the reaction resulting in the production of hydrogen peroxide would seem to bring about an increase in both reactions (2) and (3) as proposed by Wieland. Such a decrease in the extent of the liberation of hydrogen could be accounted for, however, on the basis of the following considerations and proposed mechanism:

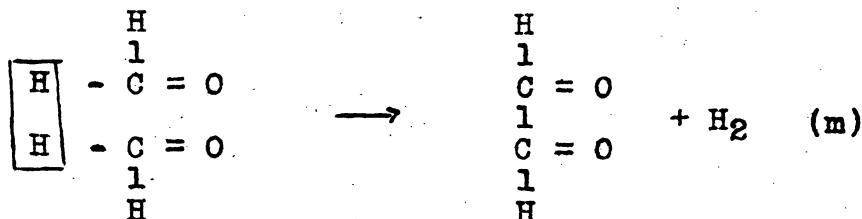
(a) Since the extent of reaction (b) is a maximum when the concentration of hydrogen peroxide is a minimum, and since hydrogen peroxide is a stronger oxidizing agent in more concentrated solutions, it is evident that in the reaction involving the liberation of hydrogen, the hydrogen peroxide does not function as a normal oxidizing agent.

(b) Hydrogen peroxide is known to be active catalytically, since, for example, it hastens the hydrolysis of cane sugar.

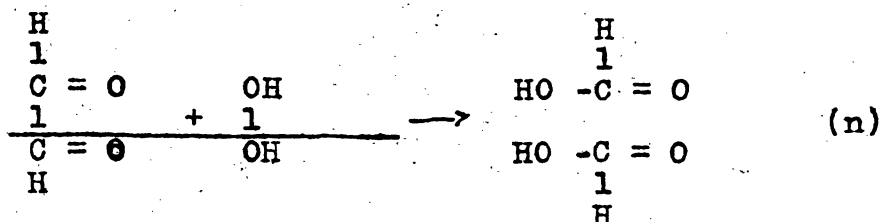
(c) Hydrogen may be liberated from formaldehyde solutions by the catalytic action of certain metals, and the same scheme of reaction is found in the completely parallel liberation of hydrogen and the linkage of two residues to yield sodium oxalate, when sodium formate is heated, thus



Therefore, it is entirely possible that the hydrogen peroxide may function catalytically in bringing about the liberation of hydrogen from two molecules of formaldehyde with the intermediate formation of glyoxal as follows:



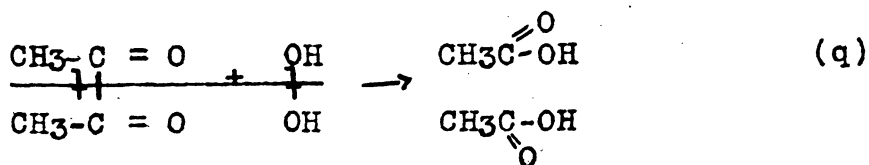
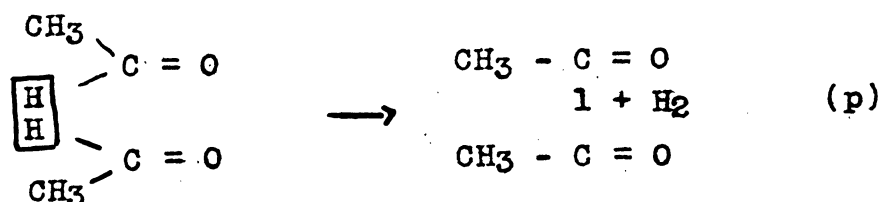
The glyoxal may then be considered as undergoing what might be termed a "perhydrolysis" reaction with hydrogen peroxide, HO-OH, comparable to "hydrolysis" with water, H-OH, giving two molecules of formic acid,



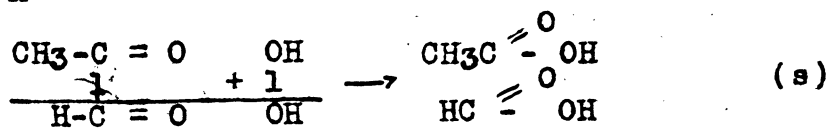
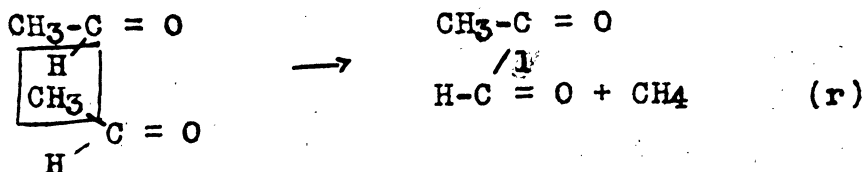
That no glyoxal was isolated may be due to the fact that the speed of the perhydrolysis reaction (n) is greater than that of preceding reaction (m).

From the experimental results it is apparent that hydrogen peroxide functions almost entirely as a normal oxidizing agent in concentrated solutions, while in dilute solutions it apparently tends to function both catalytically and what may be termed "perhydrolytically" according to equations (m) and (n) respectively.

Extending the theory, other aldehydes should behave in an analogous manner. Acetaldehyde for example, should react as follows:



There is a possibility also of another reaction in this case in which methane might be split off.



The third possibility resulting in the formation of ethane would necessitate a linkage of carbon atoms which seems highly improbable. After formulating the mechanism for the

formaldehyde reaction and extending it to acetaldehyde as was just noted, it was predicted that acetaldehyde on interaction with hydrogen peroxide should yield hydrogen or methane or both. The verification of this prediction - a substantiation of the proposed mechanism - was effected through the experimental evidence supporting the occurrence of the several reactions (p), (q), (r), and (s), subsequently recorded in experimental Part IV, section (E).

Having described the action of hydrogen peroxide upon formic acid and formaldehyde, the study of its action upon methyl alcohol naturally follows, since the products of oxidation of methyl alcohol are successively formaldehyde, formic acid, and carbonic acid.

C. Methyl Alcohol

1. Procedure

The reaction between methyl alcohol and hydrogen peroxide was found to be almost negligible at 60°C. At 100°C. however, the reaction is of such a rate that it could be studied in the same manner as the previously described reactions with formic acid and formaldehyde. It was necessary to modify the apparatus slightly, however, due to the fact that methyl formate was produced during the course of the reaction, and, being very volatile, passed through the condenser and collected in the soda-lime tubes thus interfering with carbonic acid determinations, and also causing a loss of formic acid, one of the products of the reaction.

This difficulty was overcome by introducing into the apparatus, between the condenser and the first calcium chloride tube, a Millikan wash-bottle containing concentrated sulphuric acid. These wash-bottles trapped the evolving bubbles of gas in the concentrated sulphuric acid. The methyl formate was removed almost completely by hydrolysis yielding methyl alcohol and formic acid. The latter was decomposed by the sulphuric acid, yielding carbon monoxide according to the well known reaction,



The carbon monoxide thus formed passed on into the gasometer where the quantity was determined by explosion with oxygen, and subsequent determination of the resulting carbon dioxide by absorption in sodium hydroxide according to the standard gas analysis procedure.

Due to the long period necessary for the completion of the reaction between methyl alcohol and hydrogen peroxide (24 - 48 hours), the DeKhotinsky cement sealing the reaction flasks to the condenser would tend to soften and permit thereby a leakage of gas from the apparatus. This necessitated the use of long-neck 250 cc. Kjeldahl flasks, instead of the usual short-neck reaction flasks. The necks of the Kjeldahl flasks were surrounded by copper cooling coils which kept the cement at a temperature below its softening point and thereby prevented any leakage.

The methyl alcohol used in the investigation was Merck's "C.P. free from acetone". It was tested for the presence of formaldehyde, acetone, and substances reducing permanganate and only negligible quantities were found to be present. Its specific gravity measured at 22°C. was 0.7911.

A series of four duplicate runs was conducted using one fourth mole of methyl alcohol in every case and varying the amounts of hydrogen peroxide from 1/8 to 1/4, 1/2 and 3/4 moles respectively. The volumes in each case were made up to 125 cc. as before, but the amount of sulphuric acid present was reduced from 2.16 grams, as it was in the

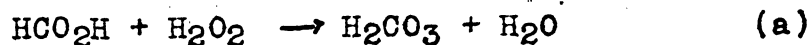
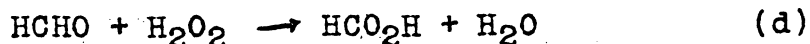
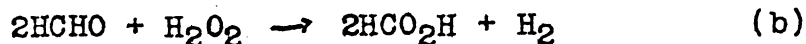
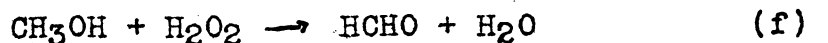
case of formic acid and formaldehyde, to 0.306 grams. The latter was done in order to speed up the reaction since it had been found previously (1) that increase in acidity of the reaction mixture, increased the stability of the hydrogen peroxide, and hence prolonged the reaction, as less peroxide was decomposed into oxygen and water.

The time for the completion of the reactions was 24, 36, 42, and 48 hours for the reactions using 1/8, 1/4, 1/2, and 3/4 moles of hydrogen peroxide respectively.

At the completion of the reactions, the gas collected was analyzed for hydrogen, oxygen, and carbon monoxide as described previously. The soda-lime tubes were weighed, and the reaction mixture was titrated for formic acid as before. The amount of formic acid found in this manner plus the amount distilling over as methyl formate, and determined from the amount of carbon monoxide found, gives the total number of moles of formic acid produced during the reaction which were not further oxidized to carbonic acid. The presence of methyl formate in the reaction mixture does not interfere with the formic acid titration with standard alkali since the methyl formate is hydrolyzed as fast as the alkali is added if the titration is conducted slowly. In other words, the methyl formate may be titrated with alkalies with the same accuracy as formic acid. In addition the mixture was analyzed for formaldehyde by the Haywood and Smith (3) modification of the Blank and Finkenbeiner (16) method.

2. Data

The results of these four determinations are given in Tables IX to XII respectively. Part A of each table records the quantity of initial reactants and the yields of the various reaction products in moles. Columns 1-4 in Part B of each table record the percentage yield of the reaction products as calculated on the basis of the following possible reactions



Column 1 gives the percentage of the total methyl alcohol oxidized no farther than the formaldehyde state according to equation (f). Column 2 gives the percentage of the total formaldehyde undergoing reaction with liberation of hydrogen according to equation (b), and Column 3 records the percentage of the total formaldehyde directly oxidized to formic acid as shown in equation (d). In Column 4 is recorded the percentage of the formic acid that is further oxidized to carbonic acid according to equation (a).

Columns 5-9, Part B, tabulate the percentage of the total hydrogen peroxide, calculated as necessary, on the basis of the above proposed reactions, to account for the yield of the various oxidation products. Thus, Column 5 gives the percentage of the initial amount of peroxide necessary to

account for the total production of formaldehyde during the course of the experiment, according to equation (f). This value includes, of course, that formaldehyde which underwent further reaction as shown by equations (b), (d), and (a). Column 6 records the percentage of the initial amount of hydrogen peroxide necessary to account for the total production of formic acid and hydrogen according to equation (b). Column 7, likewise gives the percentage of the initial amount of hydrogen peroxide necessary to bring about the yield of formic acid produced in the course of the reaction by equation (d). Column 8 gives the percent of the initial hydrogen peroxide required to produce the yield of carbonic acid obtained, as calculated on the basis of equation (a), and Column 9 gives the percent of the initial quantity of hydrogen peroxide decomposing into oxygen and water according to equation (z), i.e. the inactive hydrogen peroxide.

The last column, Number 10, Part B, in each case is a summation of the values given in Columns 5, 6, 7, 8, and 9, and should, if the reactions postulated are the only ones occurring, equal 100% within the limits of experimental error.

TABLE IX

Methyl Alcohol

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ OH moles	3 HCHO found moles	4 HCO ₂ H found moles	5 H ₂ CO ₃ found moles	6 H ₂ found moles	7 O ₂ found moles
a	.1250	.2500	.0040	.0379	.0160	.0117	.0026
b	.1250	.2500	.0034	.0375	.0162	.0125	.0026

Run	1 % yield HCHO ⇌ CH ₃ OH Eq.(f)	2 % yield H ₂ ⇌ HCHO Eq.(b)	3 % yield HCO ₂ H ⇌ HCHO (Eq.(d))	4 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq.(a)	5 % H ₂ O ₂ used ⇌ HCHO Eq.(f)
a	6.89	43.41	56.59	29.69	46.32
b	5.95	46.56	53.44	30.17	45.58

Run	6 % H ₂ O ₂ used ⇌ H ₂ Eq.(b)	7 % H ₂ O ₂ used ⇌ HCO ₂ H Eq.(d)	8 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq.(a)	9 % H ₂ O ₂ used ⇌ O ₂ Eq.(z)	10 Total % H ₂ O ₂ used
a	9.36	24.40	12.80	4.16	97.04
b	10.00	22.96	12.96	4.16	95.76

B.

TABLE X

Methyl Alcohol

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ OH moles	3 HCHO found moles	4 HCO ₂ H found moles	5 H ₂ CO ₃ found moles	6 H ₂ found moles	7 O ₂ found moles
a	.2500	.2500	.0035	.0877	.0537	.0169	.0143
b	.2500	.2500	.0033	.0898	.0509	.0180	.0148

B.

Run	1 % yield HCHO ⇌ CH ₃ OH Eq. (f)	2 % yield H ₂ ⇌ HCHO Eq. (b)	3 % yield HCO ₂ H ⇌ HCHO (eq. d)	4 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq. (a)	5 % H ₂ O ₂ used ⇌ HCHO Eq. (f)	6 % H ₂ O ₂ used ⇌ H ₂ Eq. (b)	7 % HCO ₂ H Eq. (d) ⇌ HCO ₂ H Eq. (a)	8 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq. (a)	9 % H ₂ O ₂ used ⇌ O ₂ Eq. (z)	10 Total % H ₂ O ₂ used
a	3.99	38.54	61.46	61.23	36.48	21.56	21.48	11.44	97.72	
b	3.67	40.09	59.91	56.68	37.24	21.52	20.36	11.84	98.16	

TABLE XI

Methyl Alcohol

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ OH moles	3 HCHO found moles	4 HCO ₂ H found moles	5 H ₂ CO ₃ found moles	6 H ₂ found moles	7 O ₂ found moles
a	.5000	.2500	.0023	.0319	.1119	.0288	.0594
b	.5000	.2500	.0021	.0381	.1084	.0311	.0592

B.

Run	1 % yield HCHO ⇌ CH ₃ OH Eq.(f)	2 % yield H ₂ ⇌ HCHO Eq.(b)	3 % Yield HCO ₂ H ⇌ HCHO Eq.(d)	4 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq.(a)	5 % H ₂ O ₂ used ⇌ HCHO Eq.(f)	6 % H ₂ O ₂ used ⇌ H ₂ Eq.(b)	7 % HCO ₂ H Eq.(d)	8 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq.(a)	9 % H ₂ O ₂ used ⇌ O ₂ Eq.(z)	10 Total % H ₂ O ₂ used
a	1.60	40.05	59.95	77.81	29.22	17.24	22.38	23.76	98.36	
b	1.43	42.45	57.55	74.00	29.72	16.86	21.68	23.68	98.16	

TABLE XII

Methyl Alcohol

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ OH moles	3 HCHO found moles	4 HCO ₂ H found moles	5 H ₂ CO ₃ found moles	6 H ₂ found moles	7 O ₂ found moles
a	.7500	.2500	.0008	.0313	.1611	.0354	.1149
b	.7500	.2500	.0001	.0315	.1598	.0343	.1169

B.

Run	1 % yield HCHO ⇌ CH ₃ OH Eq.(f)	2 % yield H ₂ ⇌ HCHO Eq.(b)	3 % yield HCO ₂ H ⇌ HCHO Eq.(d)	4 % yield H ₂ CO ₃ ⇌ HCO ₂ H Eq.(a)	5 % H ₂ O ₂ used ⇌ HCHO Eq.(f)	6 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq.(a)	7 % H ₂ O ₂ used ⇌ HCO ₂ H Eq.(d)	8 % H ₂ O ₂ used ⇌ H ₂ CO ₃ Eq.(a)	9 % H ₂ O ₂ used ⇌ O ₂ Eq.(z)	10 Total % H ₂ O ₂ used
a	0.42	36.80	63.20	83.73	25.65					
b	0.05	35.86	64.14	83.54	25.51					
a	4.72	16.31	21.48	30.64	98.80					
b	4.57	16.38	21.31	31.17	98.94					

Conclusions

The results given in Tables IX-XII verify the prediction made in Part III (c) that the reaction between methyl alcohol and hydrogen peroxide should result in the liberation of hydrogen from intermediately produced formaldehyde, according to reaction (b). The results further show that the reactions (a), (b), (d), shown to occur when hydrogen peroxide reacts with formaldehyde, also take place when hydrogen peroxide reacts with methyl alcohol, the three reactions being preceded by the direct oxidation of methyl alcohol to formaldehyde, equation (f). The ease of oxidation of formaldehyde is shown by the fact that only very small quantities of the latter remained in the reaction mixture at the end of the reaction.

Reaction (b), it will be noted, decreases in extent with increase in hydrogen peroxide concentration as in the case of formaldehyde. It should be noted, however, that reaction (d) always predominates even in the dilute solutions, and furthermore the change with concentration is only very slight as compared with the corresponding values for pure formaldehyde. This difference probably owes its explanation to the fact that the speed of reaction (f) is less than that of any of the other reactions occurring. Thus the concentration of formaldehyde at any given time during the greater part of the reaction is much less than the concentration of the hydrogen peroxide, and hence reaction (d) predominates.

Only toward the end of the reaction do the concentrations of peroxide and formaldehyde approach conditions of approximate equality, where reaction (b) would begin to predominate.

Reactions (a) and (z) increase, as would be expected, with increasing concentrations of hydrogen peroxide.

Columns 10, Part B, in each case show the close agreement of the initial amount of hydrogen peroxide with that calculated on the basis of the proposed reactions from the yield of reaction products. These data indicate conclusively that the reactions proposed take place to the extent noted in Columns 1-4, Part B of each table.

Having considered the extent of the occurrence of the reactions between formaldehyde and a series of the simple carbon compounds containing one carbon atom - namely, formic acid, and methyl alcohol - the study was extended to acetic acid and acetaldehyde with a view to further confirm the proposed reaction mechanism.

D. Acetic Acid

1. Procedure

Using the apparatus as described in the preceding Part C, with the exception that the Millikan wash-bottle was removed, the action of hydrogen peroxide upon acetic acid was studied. The reaction was found to proceed much more slowly than the corresponding reaction with formic acid, but was much more rapid and complete than would be expected of such a stable compound as acetic acid. The reaction between one fourth mole of acetic acid and one half mole of hydrogen peroxide in 125 cc. of solution containing .306 grams of sulphuric acid, was complete after 18 hours heating in the water bath at 100°C.

The gas collected was found to contain no hydrogen, methane, or carbon monoxide. The reaction mixture contained in addition to unaffected acetic acid, formic acid, but no formaldehyde. The presence of glycolic acid or glyoxylic acid could likewise not be established. Carbonic acid was determined in the described manner.

The acetic acid and formic acid were determined together by titration with standard alkali. The formic acid was then determined gravimetrically by the mercuric chloride method. In this method, to 10 cc. aliquot portions of the reaction mixture contained in 250 cc. Erlenmeyer flasks, were added 40 cc. of a 5% mercuric chloride solution and 5 grams of sodium acetate. The flasks were then heated

on a boiling water bath for two hours, during which time the mercuric chloride was quantitatively reduced by the formic acid, to the insoluble mercurous chloride according to the equation,



The mercurous chloride was filtered onto a Gooch crucible washed with hot water, alcohol and ether and dried at 105° to constant weight.

2. Data

Table XIII gives the results obtained on duplicate runs conducted as above, using one fourth mole of acetic acid and one half mole of hydrogen peroxide. Since only formic acid and carbonic acid were isolated as reaction products, the hydrogen peroxide equivalents recorded in Columns 6 and 7 are based on the following reactions respectively.

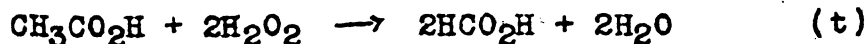


TABLE XIII

Acetic Acid

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ COOH moles	3 HCO ₂ H found Eq. (t) moles	4 H ₂ CO ₃ found Eq. (u) moles	5 % oxidation CH ₃ COOH → HCO ₂ H + CO ₂ (Eq. t+u)
a	.5000	.2500	.0100	0.0733	16.68
b	.5000	.2500	.0101	0.0766	17.36
Run	6 H ₂ O ₂ ⇌ HCO ₂ H Equa. (t) moles	7 H ₂ O ₂ ⇌ H ₂ CO ₃ Equa. (u) moles	8 H ₂ O ₂ ⇌ O ₂ Equa. (z) moles	9 Total H ₂ O ₂ (6, 7, & 8) moles	
a	.0100	.1466	.3240	.4806	
b	.0101	.1532	.3180	.4813	

3. Conclusions

The results recorded in Table XIII indicate that acetic acid is oxidized by hydrogen peroxide to carbonic acid with the intermediate production of formic acid. Direct evidence that the oxidation proceeds through glycolic and glyoxylic intermediate stages is lacking since neither of these compounds could be isolated. It is entirely probable, however, that these compounds are produced in the course of the reaction and are immediately oxidized, since both are readily susceptible to oxidation.

The stability of the acetic acid toward oxidation is shown by Column 5, from which it is seen that only approximately 17% of the acetic acid underwent oxidation in the presence of double the molar quantities of hydrogen peroxide.

These results are pertinent since they indicate that acetaldehyde which is studied subsequently should be oxidized by hydrogen peroxide to some extent beyond acetic acid.

E. Acetaldehyde

1. Procedure

Owing to the difficulty involved in working with acetaldehyde due to its volatility, the polymerized form, paraldehyde, was used in this investigation. Eastman's C.P. paraldehyde was redistilled and the portion of constant boiling point 124°C . was used. Since the paraldehyde is depolymerized on heating with dilute sulphuric acid, the former afforded a convenient method of introducing into the reaction mixture definite amounts of acetaldehyde in the paraldehyde state, and at the same time avoiding the difficulties involved in conducting a reaction at 100°C . with the very volatile acetaldehyde. Even with this precaution it was again necessary to modify the apparatus because small amounts of the acetaldehyde formed during depolymerization of the paraldehyde, would collect in the soda-lime tubes and thereby interfere with the carbonic acid determinations. The use of a Millikan wash-bottle containing sulphuric acid, as used in the case of methyl alcohol, was not satisfactory owing to the fact that the acetaldehyde collecting in the acid was immediately polymerized with subsequent dehydration, apparent carbonization and liberation of sulphur dioxide. This difficulty was overcome by the introduction of a second Millikan wash-bottle containing ethyl alcohol before the one containing sulphuric acid.

The alcohol easily removed the acetaldehyde vapors while the sulphuric acid was efficient in removing any of the alcohol carried over by the stream of evolving gases.

Three sets of duplicate runs were conducted using one fourth of a mole of paraldehyde in each case, varying the quantity of hydrogen peroxide from $1/8$ to $1/4$, and $1/2$ mole in solutions of 125 cc. volume and containing 0.306 grams of sulphuric acid.

The time required for the completed reaction varied from 18 to 24 hours, which was much greater than would be expected with so easily an oxidizable substance. At the completion of the reaction, the reaction mixture was analyzed for formic acid and acetic acid together by titration with standard alkali as in previous cases. The formic acid was determined by the mercuric chloride method as before, and the acidity found thusly to be due to formic acid when subtracted from the total acidity, gave the yield of acetic acid.

The yield of gaseous products was analyzed for hydrogen, oxygen, methane, and carbon monoxide. No carbon monoxide was present but hydrogen, methane, and oxygen were quantitatively determined. Oxygen was determined in the usual manner while the hydrogen and methane was obtained together by explosion and subsequent removal of the carbon dioxide thus produced, by absorption in sodium hydroxide. Since no carbon monoxide was present, the decrease in volume

on absorption in sodium hydroxide gave the percentage of methane in the sample of gas. Two thirds of the value obtained by subtracting twice this percentage of methane from the decrease in volume on explosion gave the percentage of hydrogen in a 100 cc. sample. In order to prove that the compound producing carbon dioxide was methane, the amount of oxygen consumed in the explosion was calculated from a determination of the oxygen present before and after explosion. The amount of oxygen thus found corresponded in every case to within three percent of the calculated value for a mixture of hydrogen and methane.

The production of both hydrogen and methane as products of the action of hydrogen peroxide upon acetaldehyde was predicted through the extension of the reaction mechanism. (Equations (m) and (n) in the case of formaldehyde, to the analogous behavior of acetaldehyde (Equations (p), (q), (r), and (s)).

2. Data

The data for the three duplicate runs described in (1) above is found in Tables XIV, XV, and XVI. Part A of each table records the initial quantities of hydrogen peroxide and acetaldehyde, together with the molar yields of the various reaction products.

In Part B of each table, Columns 1-3 indicate the

percentages of the total acetaldehyde reacting according to the three equations (j), (k), and (l) respectively. Thus Column 1 records the percent of the total acetaldehyde undergoing reaction with the liberation of hydrogen as shown in equation (j). Column 2 gives the percent of the total acetaldehyde reacting to produce methane according to equation (k), while Column 3 records the percentage of the total acetaldehyde directly oxidized to acetic acid as shown by equation (l).

Columns 4-9, Part B, tabulate the percentage of the total hydrogen peroxide calculated as necessary on the basis of the proposed reactions, to account for the yields of the various products. Thus Column 4 indicates the percentage of the initial amount of hydrogen peroxide necessary to account for the total extent of reaction (j), as measured by the yield of hydrogen. Column 5 gives likewise the percentage of the initial amount of hydrogen peroxide necessary to account for the total extent of reaction (k), as measured by the yield of methane. Column 6 shows the percentage of the initial quantity of hydrogen peroxide necessary to bring about the yield of acetic acid produced in the course of the reaction according to reaction (l). These values include, of course, the acetic acid which subsequently underwent further reaction according to reactions (t) and (a). In Column 7 is given the percent of

the hydrogen peroxide initially used, which would be necessary to produce the total amount of formic acid formed during the course of the reaction by equation (t). This latter value includes likewise the formic acid which was further oxidized to carbonic acid as shown by equation (a). Column 8 records the total percentage of the initial hydrogen peroxide necessary to produce the yield of carbonic acid obtained according to equation (a), while Column 9 gives the percent of the initial quantity of peroxide decomposing into molecular oxygen and water.

The last column, number 10, in each case is a summation of the values given in Columns 4-9, and should approximate 100% if all of the reaction products have been accounted for.

TABLE XIV

Acetaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ CHO moles	3 CH ₃ CO ₂ H found Eq. (l) moles	4 HCO ₂ H found Eq. (k+t) moles	5 H ₂ CO ₃ found Eq. (a) moles	6 H ₂ found Eq. (j) moles	7 CH ₄ found Eq. (k) moles	8 O ₂ found Eq. (z) moles
A	.1250	.2500	.0670	.0081	.0183	.0021	.0032	.0084
b	.1250	.2500	.0710	.0099	.0172	.0017	.0023	.0027

B.

Run	1 % yield CH ₃ CHO Eq. (j)	2 % yield CH ₄ CH ₃ CHO Eq. (k)	3 % yield CH ₃ CO ₂ H CH ₃ CHO Eq. (d)	4 % H ₂ O ₂ used H ₂ Eq. (j)	5 % H ₂ O ₂ used CH ₄ Eq. (k)	6 % H ₂ O ₂ used CH ₃ CO ₂ H Eq. (y)	7 % H ₂ O ₂ used HCO ₂ H Eq. (t)	8 % H ₂ O ₂ used H ₂ CO ₃ Eq. (a)	9 % H ₂ O ₂ used O ₂ Eq. (z)	10 Total % H ₂ O ₂ used
a	2.56	3.91	93.53	1.68	2.56					
b	2.00	2.69	95.31	1.36	1.74					
a	45.60	18.56	14.64	13.44	96.48					
b	55.40	19.84	13.76	4.32	96.40					

TABLE XV

Acetaldehyde

A.

Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ CHO moles	3 CH ₃ CO ₂ H found Eq. (l) moles	4 HCO ₂ H found Eq. (k+t) moles	5 H ₂ CO ₃ found Eq. (a) moles	6 H ₂ found Eq. (j) moles	7 CH ₄ found Eq. (k) moles	8 O ₂ found Eq. (z) moles
a	.2500	.2500	0.1422	.0075	.0211	.0044	.0026	.0124
b	.2500	.2500	0.1422	.0078	.0231	.0038	.0022	.0122

B.

Run	1 % yield CH ₃ CHO Eq. (j)	2 % yield CH ₄ CH ₃ CHO Eq. (k)	3 % yield CH ₃ CHO Eq. (l)	4 % H ₂ O ₂ used H ₂ Eq. (j)	5 % H ₂ O ₂ used CH ₄ Eq. (k)	6 % H ₂ O ₂ used HCO ₂ H Eq. (t)	7 % H ₂ O ₂ used HCO ₂ H Eq. (t)	8 % H ₂ O ₂ used H ₂ CO ₃ Eq. (a)	9 % H ₂ O ₂ used O ₂ Eq. (z)	10 Total % H ₂ O ₂ used
a	2.79	1.65	95.56	1.76	1.04			9.92	86.36	
b	2.40	1.39	96.21	1.52	0.88			9.76	87.04	

TABLE XVI

Acetaldehyde

A.

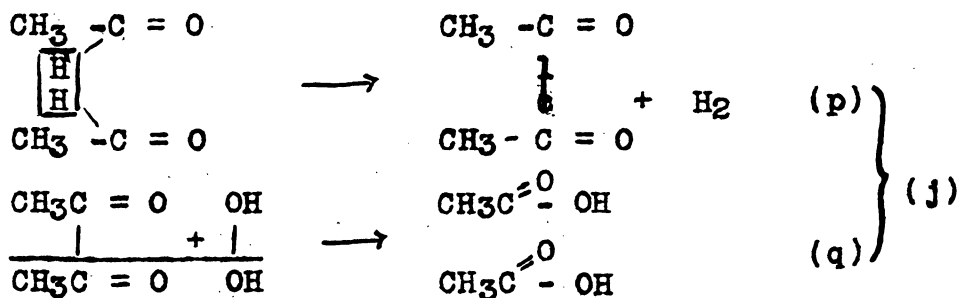
Run	1 Initial H ₂ O ₂ moles	2 Initial CH ₃ CHO moles	3 CH ₃ CO ₂ H found Eq. (z)	4 HCO ₂ H found Eq. (k+t) moles	5 H ₂ CO ₃ found Eq. (a)	6 H ₂ found Eq. (j) moles	7 CH ₄ found Eq. (k) moles	8 O ₂ found Eq. (z) moles
a	.5000	.2500	.1870	.0082	.0444	.0035	.0007	.0773
b	.5000	.2500	.1775	.0080	.0471	.0036	.0006	.0792

B.

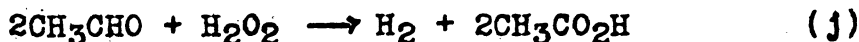
Run	1 % yield CH ₃ CHO Eq. (j)	2 % yield CH ₃ CHO Eq. (k)	3 % yield CH ₃ CHO Eq. (l)	4 % H ₂ O ₂ used Eq. (j)	5 % H ₂ O ₂ used Eq. (k)	6 % H ₂ O ₂ used Eq. (t)	7 % H ₂ O ₂ used Eq. (z)	8 % H ₂ O ₂ used Eq. (a)	9 % H ₂ O ₂ used Eq. (z)	10 Total % H ₂ O ₂ used
a	1.66	0.33	98.01	0.70	0.14					87.84
b	1.75	0.30	97.95	0.72	0.12					87.52
a	36.82	10.38	8.88	30.92	87.84					
b	34.68	10.90	9.42	31.68	87.52					

Conclusions

The data given in Tables XIV-XVI verify the prediction made in Section B, Part IV, Formaldehyde, that the action of hydrogen peroxide upon acetaldehyde should result in the liberation of both hydrogen and methane, and indicate that the following mechanism proposed in that section, is correct. The liberation of hydrogen is pictured as follows:

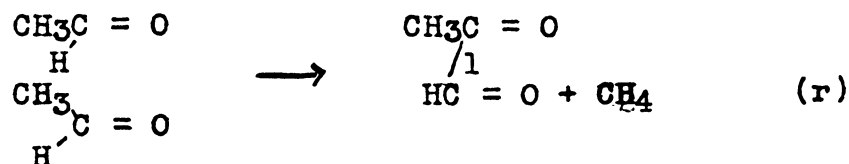


The summation of equations (p) and (q) gives equation (j)

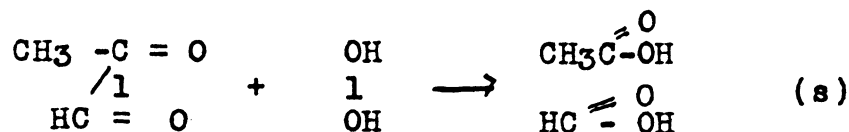


This reaction is perfectly analogous to the liberation of hydrogen from formaldehyde (equation b). The catalytic action of the hydrogen peroxide brings about a joining of two molecules of acetaldehyde with a liberation of one molecule of hydrogen. The diacetyl thus formed undergoes perhydrolysis as shown in equation (p), giving two molecules of acetic acid.

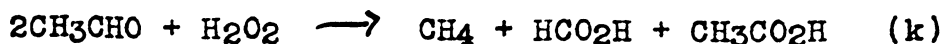
The liberation of methane is pictured similarly with methane splitting out instead of hydrogen.



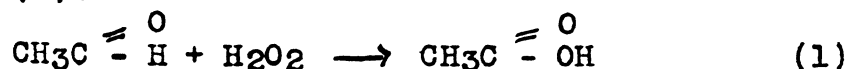
The methyl glyoxal thus formed undergoing perhydrolysis into one molecule of acetic acid and one molecule of formic acid as follows:



The summation of equations (r) and (s) gives equation (k)



Concurrent with the above reactions is the direct oxidation of acetaldehyde to acetic acid according to equation (1).



It will be noted in Tables XIV-XVI that reaction (1) is by far the predominant reaction of the three, nearly 95% of the total acetaldehyde undergoing this reaction where the hydrogen peroxide-acetaldehyde molar ratio is 1-2. At this concentration the extent of reaction (k) is slightly greater than that of reaction (j).

Increase in the concentration of hydrogen peroxide produces an increase in the extent of reaction (1) as shown by Tables XV and XVI. This is in conformity with the results obtained with formaldehyde and methyl alcohol, although with acetaldehyde the increase is not so marked. Reaction (k) decreases markedly with increasing peroxide concentration

while reaction (j) at first increases as shown in Table XV, and then falls off as shown in Table XVI.

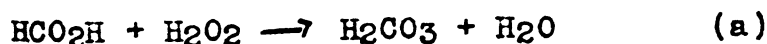
The further oxidation of acetic acid to formic acid and carbonic acid increases as would be expected with increasing hydrogen peroxide concentrations.

It will be noted from Columns 10 in Tables XV and XVI that the total hydrogen peroxide accounted for from the yield of oxidation products is only approximately 88% of the initial peroxide used. This deviation can only be explained as being due to the formation of intermediate products of the reaction whose isolation was not effected in the experimental procedure employed. This fact, however, has no effect upon the interpretation of the mechanism of the reaction for the liberation of hydrogen and methane.

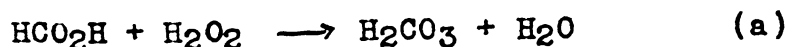
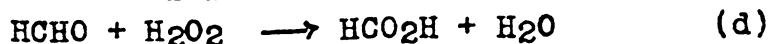
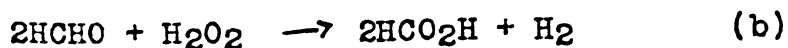
GENERAL SUMMARY AND CONCLUSIONS

The study of the nature and extent of the action of hydrogen peroxide upon simple carbon compounds has led to the postulation of the occurrence of a variety of reactions, the equations for which have been verified by the experimental data, with respect not only to the yields of the products obtained, but also to the quantities of hydrogen peroxide participating in the reactions. The general summary, proposed mechanism for reactions, and conclusions are as follows.

A. Formic acid has been shown to be oxidized directly to carbonic acid by hydrogen peroxide in slightly acid solution at 100°C. in conformity with the equation



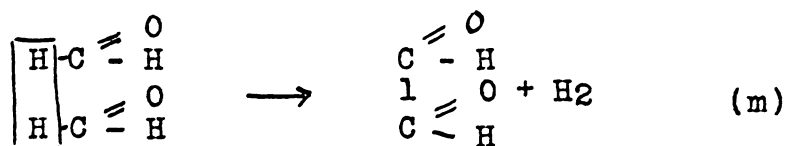
B. The reaction between formaldehyde and hydrogen peroxide in slightly acid media at 60° has been studied and the following reactions have been shown to take place:



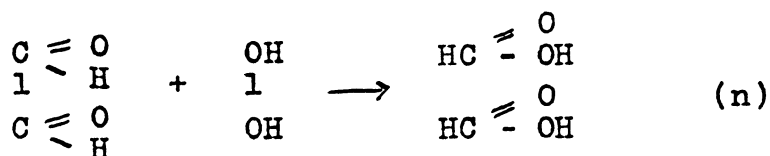
Reactions (b) and (d) are concurrent, each being followed to a greater or lesser extent, depending upon the hydrogen peroxide concentration, by reaction (a). Reaction (b) has been found to predominate at low hydrogen peroxide concentrations, while reaction (d) predominates where the hydrogen

peroxide concentration is high.

A mechanism has been proposed to explain the liberation of hydrogen according to reaction (b) on the basis of the catalytic liberation of one molecule of hydrogen from two molecules of formaldehyde as follows,

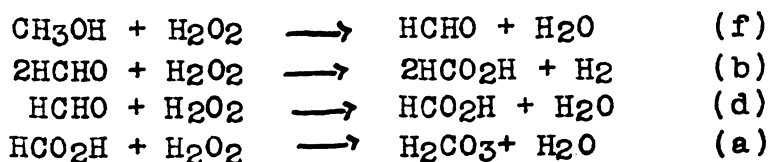


This reaction is followed by a perhydrolysis of the intermediately formed glyoxal,



the speed of the latter reaction (n) being greater than that of the former (m).

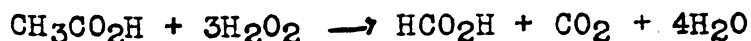
C. The action of hydrogen peroxide on methyl alcohol in slightly acidic media at 100°C. has been studied and the following reactions have been shown to be concurrent.



The scheme of the reaction has been explained on the same basis as the reactions occurring in the case of formaldehyde with the addition of reaction (f), the direct oxidation of methyl alcohol to formaldehyde. Concerning the two

reactions between formaldehyde and hydrogen peroxide, (b) and (d), (d) has been shown to be the predominant one at all concentrations of hydrogen peroxide studied. This has been explained by the fact that reaction (f) proceeds so slowly in comparison with the other reactions that the formaldehyde concentration at any time during the course of the reaction is very low. Reaction (d) has been shown to increase with increased concentration of peroxide as in the case of formaldehyde.

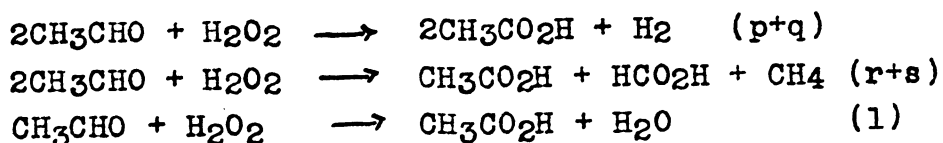
D. The reaction between acetic acid and hydrogen peroxide in slightly acid aqueous solutions at 100°C. has been shown to take place very slowly, with the formation of formic acid and carbonic acid, probably in accordance with the following equation:



The intermediate production of glycolic and glyoxylic acids could not be established although it is probable that the reaction proceeds through these successive stages.

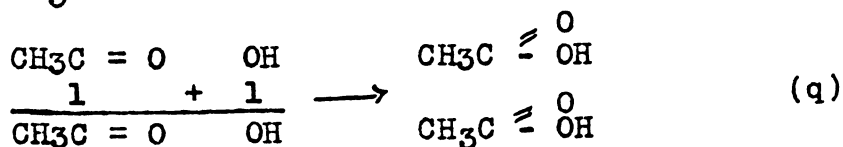
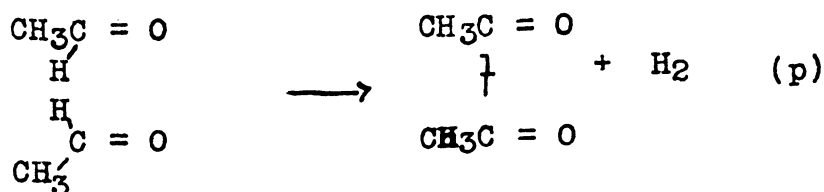
E. With a view toward verifying the mechanism proposed to explain the liberation of hydrogen from formaldehyde, the action of hydrogen peroxide upon acetaldehyde in slightly acid solution at 100°C. was studied. The reaction was found to liberate both hydrogen and methane in accordance with the proposed mechanism. The following reactions have been shown to be concurrent, each being followed to some extent by the oxidation of acetic acid as

shown in preceding part D above.

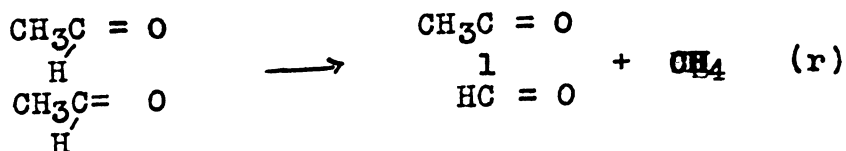


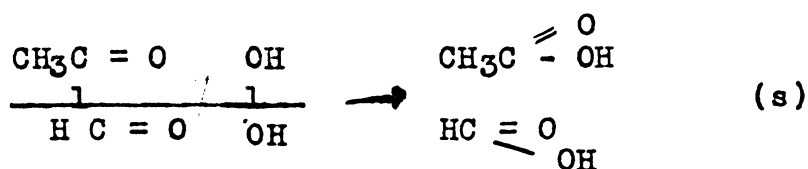
Reaction (1) has been found to be the predominant reaction in all cases. Reactions (p+q) and (r+s) decrease in extent with increase in hydrogen peroxide concentration, reaction (r+s) being slightly greater in the more dilute solutions, while reaction (p+q) is more extensive than (r+s) in the more concentrated solutions of peroxide.

The reaction mechanism proposed to explain the liberation of hydrogen from formaldehyde by hydrogen peroxide has been extended to acetaldehyde analogously to formaldehyde. The liberation of hydrogen is explained as follows:



while the liberation of methane is pictures in a similar manner:





These experimental results obtained with acetaldehyde confirm the proposed reaction mechanism.

The observations of this study clearly show that hydrogen peroxide displays some very remarkable properties which are apparently abnormal, or to say the least, entirely unexpected. For instance on reaction with formaldehyde, it not only gives the normally expected reaction, namely direct oxidation to formic acid ($\text{HCHO} + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O}$) but also, contrary to expectation, yields hydrogen ($2\text{HCHO} + \text{H}_2\text{O}_2 \rightarrow 2\text{HCO}_2\text{H} + \text{H}_2$)

This abnormal behavior has been explained by the proposed reaction mechanism involving perhydrolysis, but it should be noted as possibly significant that this latter reaction finds somewhat of a parallel in the Cannizzaro reaction with formaldehyde, namely



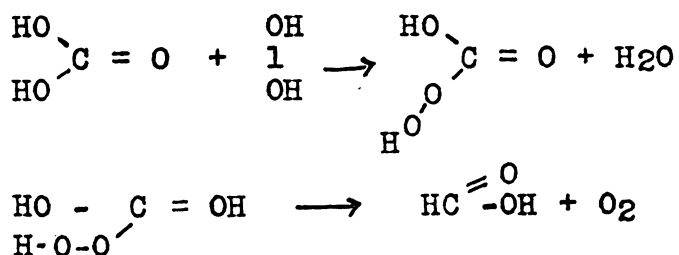
wherein one molecule of formaldehyde is oxidized to formic acid and another molecule of formaldehyde is reduced to methyl alcohol. In other words when hydrogen peroxide reacts with formaldehyde there is an oxidation product, formic acid, and a reduction product, hydrogen. Similarly when formaldehyde reacts with sodium hydroxide, there results the same oxidation product, formic acid, but the

reduction product is methyl alcohol. Another research now in progress in this laboratory dealing with the mechanism of the Cannizzaro reaction will further emphasize this parallel.

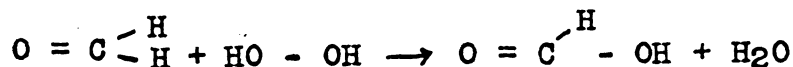
In further relation to the proposed reaction mechanism it is of interest to note that it affords a direct explanation of a similar abnormal action of hydrogen peroxide in reducing carbonic acid to formic acid with the liberation of oxygen according to the equation:



The following scheme illustrates the application of the proposed perhydrolysis mechanism to this reaction:



In fact the perhydrolysis mechanism may serve to explain the normal oxidizing reactions of hydrogen peroxide. For example when formaldehyde is oxidized directly to formic acid, the perhydrolysis may be represented thus,



Reactions of this type involving perhydrolysis may very likely occur in photosynthetic processes.

ACKNOWLEDGMENT

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Appreciation is also expressed to Dr. H. R. Carveth, President of the Roessler and Hasslacher Chemical Company, Niagara Falls, New York, who generously donated the hydrogen peroxide used throughout in the experimental work.

BIBLIOGRAPHY

1. The Action of Hydrogen Peroxide on Methyl Alcohol in Acid and Basic Solution.
Payne, U.C. Thesis, 1928.
2. Kastle & Loevenhart, J.Am.Chem.Soc. 21, 262 (1899)
3. Kastle & Loevenhart, Am.Chem.J. 29, 424 (1903)
4. Battelli, Compt. Rend. 138, 651 (1904)
5. Dakin, J.Biol.Chem. 4, 227 (1908)
6. Holden & Hatcher, Trans.Roy.Soc.Can. 18, III, 231 (1924)
7. Wislicenus, Ber. 51, 942 (1918)
8. Rupp & Schlee, Biochem.Zeit. 172, 373 (1926)
9. Geisow, Ber. 37, 515 (1904)
10. Lyford, J.Am.Chem.Soc. 29, 1227 (1907)
11. Cervello and Pitini, Gazz. 37 1, 577 (1907)
12. Bach & Generosov, Ber. 55 B, 3560 (1922)
13. Wieland & Wingler, Ann. 43, 30 (1923)
14. Hatcher and Holden, Trans.Roy.Soc.Can. 20, 395 (1926)
15. Renard, Ann.Chem.Phys. 5, 335 (1879)
16. Blank and Finkenbeiner, Ber. 31, 2279 (1898)
17. Frankforter and West, J.Am.Chem.Soc. 27, 718 (1905)
18. Heimrod and Levene, Biochem.Z. 29, 31 (1910)
19. Schmiedel, Pharm. Zentralhalle 54, 709 (1913)
20. Doroshevskii and Bardt, J.Russ.Phys.Chem.Soc. 46, 754 (1914)
21. Dakin, J.Biol.Chem. 4, 77 (1908)
22. Knoop and Gehrke, Z.Physiol.Chem. 146, 63 (1925)

23. Walton & Christiansen, J.Am.Chem.Soc. 48, 2083 (1926)
24. Baeyer and Villiger, Ber. 33, 2484 (1900)
25. Reiner, Z.Anorg.Allgem.Chem. 141, 363 (1925)
26. Hatcher and Toole, Trans.Roy.Soc.Can. 20, 415 (1926)
27. Traube, Ber. 16, 123 (1883)
28. Legler, Ber. 18, 3347 (1885)
29. Wieland, Ber. 45, 484, 679, 2606 (1912)
Ber. 46, 3327 (1913)
Ber. 47, 2085 (1914)
Ber. 54, 2353 (1921)
30. Haywood and Smith, J.Am.Chem.Soc. 27, 1183 (1905)

