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I hereby recommend that the thesis prepared under my supervision by Eric Bergman

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be accepted as fulfilling this part of the requirements for the degree of Ph. D.

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A QUANTITATIVE STUDY OF THE REACTIVITIES OF SIMPLE CARBON-NITROGEN COMPOUNDS WITH HYDROGEN PEROXIDE

A dissertation submitted to the
Graduate School
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by

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CONTENTS

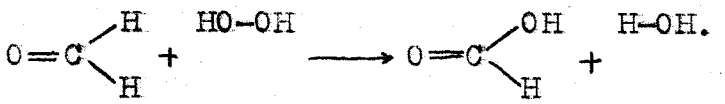
INTRODUCTION

The research to be discussed in this thesis is a continuation of the work started in this laboratory in 1927 on the action of hydrogen peroxide on simple carbon compounds. The first work [1], carried out by J. H. Payne to determine the effect of variations in the acidity of the medium upon the oxidation of methyl alcohol by hydrogen peroxide, disclosed some startling facts. The amounts of oxidation products which were recovered were invariably greater than the amounts calculated from the reactions known to occur. Since the reactions investigated were conducted in a closed system, so that the amount of hydrogen peroxide added and also that which had decomposed to give oxygen were accurately known, the only way to account for the variation was to assume that simultaneously with the oxidation reaction, involving hydrogen peroxide, there were other reactions occurring which involved the formation of reducing substances whose presence had escaped notice. This speculation was verified by the discovery of hydrogen as one of the reaction products.

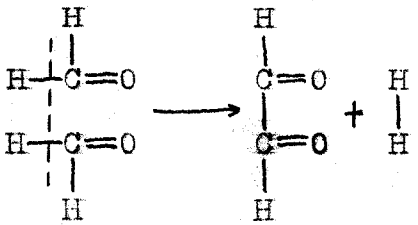
This unsuspected formation of hydrogen had never before been recorded in the literature, and it led to a quantitative investigation of the reactions of methyl alcohol, formaldehyde, and formic acid with hydrogen peroxide, with the view of suggesting a possible mechanism for the reaction [2]. In each case the products of the reaction were quantitatively determined, and the amounts of hydrogen peroxide equivalent

to the amounts of the oxidation products, as calculated from the reactions proposed, were found to agree with the actual quantities of hydrogen peroxide used, within the limits of experimental error.

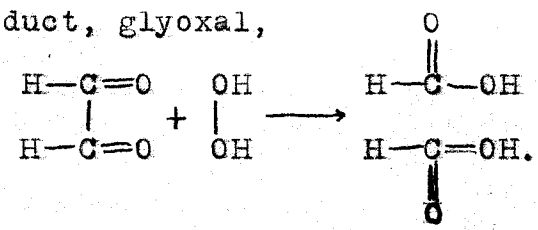
In order to explain this unusual formation of hydrogen, as well as the usual oxidation reactions, a new type of reaction mechanism was proposed. It was called " perhydrolysis ", and was defined as " a double decomposition reaction involving hydrogen peroxide in precisely the same manner that hydrolysis is a double decomposition reaction involving water." Thus for the normal oxidation of formaldehyde to formic acid, the equation may be written



To explain the reaction of formaldehyde to give formic acid and hydrogen required the additional assumption that hydrogen peroxide may act catalytically to liberate hydrogen.



This is immediately followed by the perhydrolysis of the intermediate product, glyoxal,



These two reactions may be summarized as one equation,

$$2\ HCHO + H_2O_2 \longrightarrow H_2 + 2\ HCOOH.$$

This proposed mechanism has been confirmed by the quantitative data obtained in the cases of formaldehyde, methyl alcohol, formic acid, acetaldehyde, acetic acid, glycollic acid, and lactic acid [2,3].

The investigation to be described in the following paper was undertaken in order to study the reactions of simple carbon-nitrogen compounds with hydrogen peroxide, and to determine if the mechanism described above could be applied to their reactions. The compounds selected for this purpose were (A) ethanol amine, (B) urea, (C) acetonitrile, (D) nitromethane, (E) glycine, and (F) hydrogen cyanide.

An historical review of previous work recorded in the literature in relation to each of the above-mentioned carbon-nitrogen compounds will be presented, followed by the experimental procedure employed and the interpretation of the results.

HISTORICAL

A. Ethanol Amine

This compound was chosen as the first one to be investigated because it possessed both an alcohol grouping and a primary amine group. Since alcohols are very susceptible to oxidation, there should be no trouble in obtaining some reaction between ethanol amine and hydrogen peroxide. An extensive search of the literature revealed that very little work has been done on the oxidation of ethanol amine.

Suto [4] studied the action of hydrogen peroxide on a sulfuric acid solution of ethanol amine, to which he added a crystal of ferrous sulfate as catalyst. He identified a small amount of glyoxal as one of the products, proving its presence by means of the melting point and nitrogen content of its osazone. The solution had a strong reducing action on Fehling's solution. Suto mentions no other products, and does not say whether the glyoxal caused the reduction, or whether some other product is responsible. Certainly ammonia and carbon dioxide must have been formed, although he makes no mention of them. The formation of glyoxal may be explained by applying the perhydrolysis mechanism, but before this is done it must be assumed that the amino group is hydrolyzed off, and a hydroxyl radical has replaced it. This may be written thus:

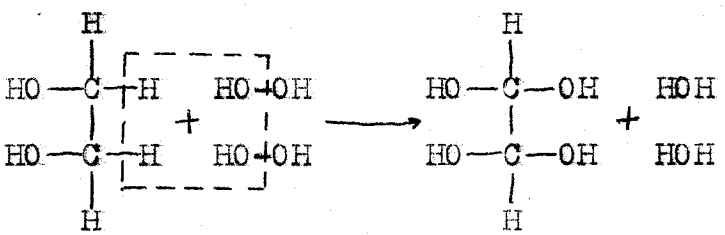
$$CH_2OH\text{-}CH_2NH_2 + H_2O \longrightarrow CH_2OH\text{-}CH_2OH + NH_3,$$

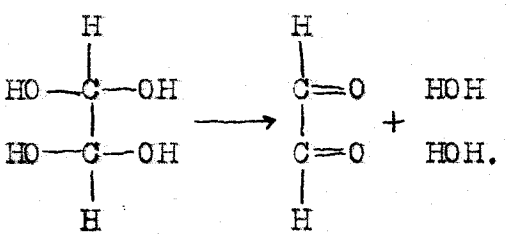
and

$$CH_2OH\text{-}CH_2NH_2 + H_2O_2 \longrightarrow CH_2OH\text{-}CH_2OH + NH_2OH.$$

The formation of hydroxylamine is extremely unlikely; no worker has ever reported its formation in any reaction of this type. It is likely that the deamination occurs by hydrolysis, catalyzed by hydrogen peroxide.

The ethylene glycol may then be oxidized through perhydrolysis as follows:





Summing up the hydrolysis of ethanol amine to glycol and the two perhydrolysis reactions, we have

$$\begin{matrix} CH_2NH_2 \\ | \\ CH_2OH \end{matrix} + 2\ H_2O_2 \longrightarrow NH_3 + \begin{matrix} H\text{—}C{=}O \\ | \\ H\text{—}C{=}O \end{matrix} + 3\ H_2O.$$

In the presence of excess hydrogen peroxide the glyoxal would immediately undergo further oxidation to yield formic acid, and finally carbonic acid.

$$\begin{matrix} CHO \\ | \\ CHO \end{matrix} + \begin{matrix} OH \\ | \\ OH \end{matrix} \longrightarrow \begin{matrix} HCOOH \\ \\ HCOOH \end{matrix} \quad ; \quad \begin{matrix} COOH \\ | \\ H \end{matrix} + \begin{matrix} OH \\ | \\ OH \end{matrix} \longrightarrow \begin{matrix} COOH \\ | \\ OH \end{matrix} + HOH$$

To summarize, ethanol amine should yield first of all glycol and ammonia, then glyoxal, formic acid, and finally carbonic acid.

B. Urea

An investigation of the literature on urea revealed numerous reports and patents on the use of this compound in mixture with hydrogen peroxide as a convenient source of solid hydrogen peroxide, some of which will be noted.

Tanatar [5] studied the addition compounds of various organic compounds with hydrogen peroxide, and he was able to make a stable complex with urea which retained 15% of hydrogen peroxide for six months. Milbauer [6] describes a patent issued for a compound having 65.70% urea, 34.00% hydrogen peroxide, and 0.08% citric acid, which is reported to be very stable up to 60° C. In alcohol or water it affords a convenient source of hydrogen peroxide, and in ether it gives up the hydrogen peroxide entirely. The compound, or complex, as the case may be, has the formula $CO(NH_2)_2 \cdot H_2O_2$, containing 64.1% urea and 35.9% hydrogen peroxide. Strauss [7] describes a patent on a compound of 36% C.P. hydrogen peroxide and 64% urea, and reports that this complex is very stable.

In view of these reports it is unnecessary to try to postulate a mechanism for the oxidation; there is apparently a molecular compound formed. However, there seem to

be no references to what may happen to the urea above the decomposition temperature of the complex. The only reactions that can occur are hydrolysis to ammonium carbonate, or the production of carbonic acid and hydroxylamine by perhydrolysis. In the case of the formation of the latter, one may expect almost any stage of oxidation of nitrogen because of the marked susceptibility of hydroxylamine to oxidation.

C. Acetonitrile

The action of aqueous hydrogen peroxide on various nitriles has been of interest to several workers. Radziszewski [8] investigated the reactions of several nitriles, and he reported that in those cases where the acid amide is difficultly soluble, the reaction goes quantitatively as follows:

$$RCN + 2\ H_2O_2 \longrightarrow RCONH_2 + O_2 + H_2O.$$

He also stated that the reaction went very easily at 40° C. in an alkaline medium, but made no mention of any oxidation of any of the nitriles he studied.

Deinert [9] tried the effect of various concentrations of hydrogen peroxide solutions, and concluded that of 1.8%, 2.5%, and 8.0% solutions, the 2.5% solution gave the most satisfactory results in hydrolyzing the nitrile to the amide. He studied the effect in both the aliphatic and aromatic series.

Oliveri-Mandala [10] gives data which substantiate the equation

$$RCN + 3\,H_2O_2 \longrightarrow RCOOH + NH_3 + H_2O + 3\,O,$$

when the reaction is carried out in an alkaline medium. He found that this holds only for the aliphatic series, and that in the aromatic series there is actual oxidation, the products being derivatives of hydroxylamine and related compounds.

In no case is there any reference in the literature to the oxidation of acetonitrile by hydrogen peroxide. It will be shown subsequently that oxidation does occur.

D. Nitromethane

An exhaustive search of the literature failed to reveal any references to any work done on the reaction of nitromethane with hydrogen peroxide.

E. Glycine

The reaction between hydrogen peroxide and glycine has been of biochemical interest for some time. Dakin [11] investigated this reaction, and reported that he found copious yields of glyoxylic acid and ammonia, and also some carbon dioxide and formaldehyde. He used calculated amounts of hydrogen peroxide, added a small crystal of ferrous sulfate as catalyst, and carried out the reaction at body temperature. It is not quite clear from his writings just what he means

by " calculated amounts " of hydrogen peroxide. He writes the following reactions as possibilities:

$$NH_2CH_2COOH \begin{cases} \longrightarrow NH_3 + HCO\text{-}COOH \\ \longrightarrow NH_3 + CO_2 + HCHO \\ \longrightarrow NH_3 + CO_2 + HCOOH. \end{cases}$$

He tested for hydroxylamine, but found none.

The first action must be one of hydrolysis:

$$NH_2CH_2COOH + H_2O \longrightarrow NH_3 + CH_2OH\text{-}COOH.$$

According to the proposed perhydrolysis mechanism, the glycollic acid can then be oxidized in several ways, as described by Milstead in this laboratory [3]. The reactions which he proposed and proved to occur are summarized below:

$$CH_2OH\text{-}COOH + 2\ H_2O_2 \longrightarrow 3\ H_2O + CO_2 + HCOOH$$

$$2\ CH_2OH\text{-}COOH + 2\ H_2O_2 \longrightarrow 4\ H_2O + 2\ CO_2 + 2\ HCOOH + H_2$$

$$HCOOH + H_2O_2 \longrightarrow 2\ H_2O + CO_2.$$

Milstead found no glyoxylic acid in his solutions, and explained this fact by its extreme reactivity with oxidizing agents. Dakin did not analyze the gaseous products of his reaction, and so, if any hydrogen was formed, he did not notice its presence. As usual he failed to record the amounts of any products formed, merely referring to a " large " yield of glyoxylic acid.

Effront [12] varied his procedure by dissolving the glycine in 200 cc. of N/2 NaOH, and distilling the mixture, dropping ten-volume hydrogen peroxide into it as fast as the products distilled over. This was continued until no more ammonia was distilled out. He postulated the following reactions:

reactions:

$$NH_2CH_2COOH + H_2O \longrightarrow NH_3 + CH_2OH\text{-}COOH$$

$$CH_2OH\text{-}COOH + 2\ H_2O_2 \longrightarrow HCOOH + CO_2 + 3\ H_2O.$$

From 10 grams of glycine in this way he obtained 5.5 grams of formic acid, or 91% of theory. Most of the nitrogen was recovered as ammonia, while the remainder, 1-2%, was found as nitrate. Effront did not calculate the percentage yield of formic acid, and apparently did not isolate any other products.

Plimmer [13] studied the action of various oxidizing agents on glycine and other amino compounds. Using concentrated sulfuric and nitric acids he got small amounts of hydrogen cyanide. He writes the following equations as a possible mode of representing the reaction.

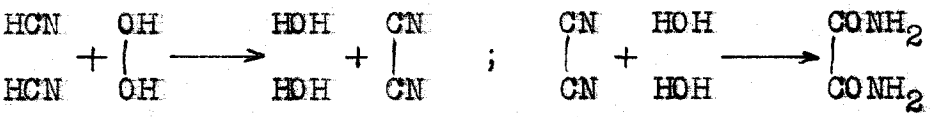
$$NH_2CH_2COOH \xrightarrow{HNO_3} HON{=}CHCOOH$$

$$HON{=}CHCOOH \longrightarrow HCN + CO_2 + H_2O$$

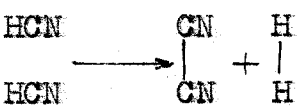
If he first hydrolyzed the acid in concentrated sulfuric acid alone, and then oxidized it, he found exactly the same amount of hydrogen cyanide. Potassium dichromate and sulfuric acid gave the same reaction. Using manganese dioxide and sulfuric acid, potassium permanganate and sulfuric acid, and sulfuric acid alone, he found little if any hydrogen cyanide as a product of the oxidation. Plimmer does not attempt to explain the differences in behaviour with different oxidizing agents, nor does he give any basis for the above equations.

E. Hydrogen Cyanide

The reaction between hydrogen cyanide and hydrogen peroxide was investigated by Attfield in 1863 [14]. He gave neither quantities nor concentrations, and said that the white insoluble product obtained was oxamide because it resembled that compound in its insolubility, lack of odor, tastelessness, etc.. Radziszewski [8] describes work on hydrogen cyanide in conjunction with that on nitriles in general. He reports quantities of oxamide, and suggests the following mechanism for its formation, which, it may be noted, involves perhydrolysis.



Cyanogen and a trace of potassium hydroxide gave him a quantitative yield of oxamide. It may be that the first of the above reactions proceeds as does the reaction of formaldehyde, previously noted, to give hydrogen, with hydrogen peroxide as a catalyst.



Radziszewski apparently did not analyze the gases formed, so that if any hydrogen had been formed he would have missed it.

Masson [15] studied extensively the reaction between potassium cyanide and hydrogen peroxide. He found it necessary to keep the solutions cool while they were being mixed, otherwise an explosion resulted. The first action was one

of oxidation:

$$KCN + H_2O_2 \longrightarrow KCNO + H_2O.$$

The remainder of the reaction involved the hydrolysis of both the potassium cyanide and potassium cyanate.

$$KCNO + 2\ H_2O \longrightarrow K(NH_4)CO_3$$

$$KCN + 2\ H_2O \longrightarrow HCOOK + NH_3$$

It was possible to account for 80% of the cyanide or peroxide, if they were present in stoichiometric amounts, as either potassium cyanate or potassium ammonium carbonate. The remainder of the cyanide and peroxide went to potassium formate, ammonia and oxygen. No oxygen was liberated until the above-mentioned 80% of the peroxide had been used to oxidize the cyanide. Masson determined the yields of cyanate, carbonate, formate, and also the initial amounts of cyanide and peroxide used in runs with varying concentrations, and from these data he was able to make the following generalizations:

1. The amount of carbonate varied directly as the peroxide used, and inversely as the cyanide used, although the relationship was not linear.
2. The amount of cyanate was inversely proportional to the carbonate, all other things being equal.
3. The sum of the carbonate, as $K(NH_4)CO_3$, and the cyanate, were practically equal to 80% of the original cyanide added.

Masson also studied the effect of the addition of quantities of free alkali and sulfuric acid to the mixture.

Free alkali added at the outset had a retarding effect on the whole reaction, diminished the amount of hydrolysis relative to the oxidation, and caused the escape of free oxygen in the early stages, whereas in the runs on neutral solutions no oxygen was evolved until all cyanide had disappeared. Ammonia added at the outset had little or no effect.

Free acid, sulfuric acid, added at the beginning retarded the whole reaction, and tended to increase the amount of hydrolysis to that of oxidation. If enough acid was added to convert all the potassium cyanide to hydrogen cyanide, Masson found that oxamide crystals formed slowly. He noted that it was necessary to allow the solutions to stand for at least 78 hours in order to get a good yield of oxamide, and did not mention any other products in this case.

From the foregoing discussion it is easy to see that the investigators all got yields of oxamide from hydrogen cyanide, and that they do not mention any other products when this is the case. One might also expect to get ammonium carbonate by ordinary hydrolysis of the prussic acid.

EXPERIMENTAL

In this section will be included the theoretical discussion of each of the compounds studied, a description of the apparatus employed, the experimental data, their interpretation, and a summary of the results.

A. Ethanol Amine

Theoretical

As has been stated in the historical section, this compound was chosen because it is both a primary alcohol and a primary amine.

One of the first actions observed to take place is the deamination of the ethanol amine to form glycol. It may be postulated that the other product be either ammonia or hydroxylamine (see above). Since ammonia was apparently the only product of this reaction, the formation of hydroxylamine will not be considered. The equation for this hydrolysis will again be noted:

$$NH_2CH_2CH_2OH + H_2O \longrightarrow CH_2OH\text{-}CH_2OH + NH_3.$$

The next step in the reaction has also been described previously, namely:

$$CH_2OH\text{-}CH_2OH + 2\,H_2O_2 \longrightarrow CHO\text{-}CHO + 4\,H_2O.$$

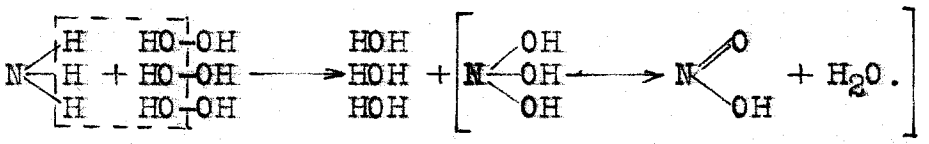
The presence of glyoxal has been proved by Suto [4]. Glyoxal may then be further oxidized by perhydrolysis, thus:

$$CHO\text{-}CHO + H_2O_2 \longrightarrow 2\ HCOOH,$$

and the formic acid formed by this reaction may also be oxidized, thus:

$$HCOOH + H_2O_2 \longrightarrow CO_2 + 2\ H_2O.$$

Then there is the possibility of a reaction between ammonia and hydrogen peroxide. Weith and Weber [16] report that solutions of ammonia are oxidized by hydrogen peroxide, the product being ammonium nitrite. This reaction may be written by perhydrolysis mechanism:



The nitrous acid so formed would immediately be neutralized by the excess ammonia to form ammonium nitrite. Weith and Weber proved the presence of ammonium nitrite, and stated that if the solution was warmed they found no nitrite, but only nitrogen, since ammonium nitrite is rapidly decomposed, thus:

$$NH_4NO_2 \longrightarrow N_2 + 2\ H_2O.$$

If some of the nitrite should be oxidized further before being decomposed, there is no reason why ammonium nitrate should not be formed.

$$HONO + H_2O_2 \longrightarrow HONO_2 + H_2O.$$

Indeed, Effront [12], in his work on glycine, did find small amounts of nitrate present in his solutions after reaction.

Since in this investigation a considerable excess of hydrogen peroxide was employed, the products to be

expected are ammonia, carbon dioxide, and perhaps small amounts of formic and nitric acids.

Apparatus and Procedure

The investigation was carried out in a closed system, as in all the previous studies in this laboratory. For this purpose it was found necessary to arrange a special absorption train which would remove as many of the components of the gases produced as was practical.

The reaction was carried out in a 500-cc. Pyrex Kjeldahl flask, which was connected to a 30-cm. upright Liebig condenser to serve as a reflux. The top of the condenser was connected to a Millikan wash-bottle containing standard sulfuric acid to absorb any ammonia liberated. The wash-bottle was connected to a U-tube filled with calcium chloride to dry the gases, and then to an Ascarite tower filled with Ascarite, for the absorption of any carbon dioxide. Following the Ascarite tower was another U-tube containing calcium chloride, which was connected to an empty gas wash-bottle, which in turn was connected to an inverted 18-liter carboy, graduated in half liters and filled with saturated sodium chloride solution. This carboy served as a gasometer to collect all the gases which were not absorbed. The gas wash-bottle immediately preceding the gasometer was so connected as to serve as a trap for any liquid which might suck back from the gasometer.

This apparatus was set up in duplicate, and the reaction flasks were placed in the same water bath, in order to make certain that the two runs would be under exactly the same conditions. Care had to be taken in order to secure two reaction flasks which were of uniform construction and which had no rough surfaces on the inner side, since it is a well-known fact that rough surfaces catalyze the decomposition of hydrogen peroxide to give oxygen according to the equation:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2. \qquad (z)$$

The connections between the flasks and the condensers and between the condensers and the tubing leading to the Millikan wash-bottles were made by tightly fitting rubber stoppers. The rest of the connections were made with pressure tubing, held in place by ligatures made of copper wire. All ground-glass joints, those in the Millikans, Ascarite towers, and gas wash-bottles, were lubricated with very heavy stop-cock grease. The glass tube from the condenser to the Millikan was broken by a 15-18 cm. mercury seal in order to allow easy manipulation of the condenser. A glass stop-cock was inserted in the stopper of each reaction vessel, and was so adjusted that the whole system could be flushed out with a stream of inert gas. All connections were tested with soap solution while the inert gas was passed through in order to make sure that there were no leaks.

The hydrogen peroxide was standardized before each run by titration with permanganate, the usual method [17] being used, except that 20 cc. were pipetted into a liter volumetric

flask, and 10-cc. aliquots were used for titration. The hydrogen peroxide used throughout this investigation was the so-called " one hundred volume ", entirely free of all organic preservatives and sulfuric acid, and was donated by the R. and H. Division, E. I. DuPont de Nemours and Co., Niagara Falls, N. Y., through the courtesy of their Dr. J. S. Reichert. It was found to be stable for an indefinite period if kept below 40° F. when not in use.

Eastman's pure ethanol amine was distilled twice, using a modified Glinsky column, and only that portion boiling between 188° and 190° C. was used. A density determination was made, in order to permit measuring the amine instead of weighing it. In this way any desired amount could be accurately measured from a calibrated burette.

One sixth of a mole of ethanol amine was run into each reaction flask, and enough hydrogen peroxide was added to give one mole, about one hundred ten cc.. The necks of the flasks were then washed down with 50 cc. of distilled water. The Millikan wash-bottled contained 200 cc. of 1.409 normal sulfuric acid, and all connections were made except those to the gasometers. The whole system was then flushed out with a stream of pure nitrogen until all residual gases had been displaced. It was later found more expedient to sweep out all the apparatus but the reaction flasks before mixing the two reagents, and to keep it closed until needed. The reaction flasks were also swept out before being used,

thus obviating the necessity for delay after the solutions had been mixed.

After all gases had been swept out the connections were made and tested, and the water bath was slowly heated to boiling. It was found necessary to perform this heating very slowly in order to allow ample time for the decomposition of the peroxide, as the solution was quite appreciably alkaline. The water bath was fitted with a gas-regulating device such that the rate of heating could be determined more accurately than was otherwise possible. After the water bath had reached the boiling point, it was maintained there until no further evolution of gas was observed. A small amount of powdered silica, to decompose the remaining peroxide, was then blown in through the stop-cocks by a stream of nitrogen, thus assuring no loss of gas. It was later found unnecessary to use the silica, as the peroxide had completely decomposed without it. The gases in the reaction flasks were then displaced by a slow stream of nitrogen, which was passed through the apparatus until the Ascarite towers had completely cooled and ample time had been allowed for removal of all other gases into the gasometers.

The increase in weight of the Ascarite towers represented the amount of carbon dioxide liberated. The contents of the Millikan wash-bottles were transferred to volumetric flasks and made up to 500cc. Ten-cc. aliquots of these solutions were titrated against standard sodium hydro-

xide, with methyl red as indicator. From these results it was possible to determine the residual acidity of the solutions, and by subtracting this from the original strength of the acid the amount of ammonia formed could be calculated.

The gases collected in the gasometers were measured, and the volumes were converted to standard conditions, corrections being made for pressure, temperature, vapor tension of saturated sodium chloride solution, and the differences in level in the gasometers. The gases proved by analysis with the Hempel apparatus to contain no combustible components, but to be mixtures of oxygen and nitrogen only. The oxygen was determined by absorption with alkaline pyrogallol, as directed by Engelder [18]. The quantity of oxygen collected was a measure of the quantity of hydrogen peroxide which did not function in the oxidation of the compound under investigation, but which decomposed directly, thus:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2. \qquad (z)$$

By subtracting the quantity of hydrogen peroxide thus directly decomposed from the initial amount used in the reaction mixture, it was possible to calculate the active hydrogen peroxide; i.e., the quantity which effected oxidation of the organic compound.

Data

Unfortunately the results obtained were not consistent. The data from repeated runs did not check. This is explained by the alkaline nature of ethanol amine;

hydrogen peroxide is very unstable in alkaline medium. Moreover, as has been noted previously, it was extremely difficult to conduct the reactions slowly enough so that the peroxide would not decompose too rapidly for the capacity of the absorption train.

In Table I are recorded the results of the two best sets of duplicate runs. It will be seen that the agreement is very poor.

Table I

Run	Amine used moles	H_2O_2 used moles	CO_2 found moles	NH_3 found moles	$O_2 \Rightarrow H_2O_2$ found moles	H_2O_2 moles	H_2O_2 active moles
I A	.167	1.000	.173	.000	.126	.252	.748
B	.167	1.000	.180	.000	.126	.252	.748
IIA	.167	1.000	.155	.00578	.218	.436	.564
B	.167	1.000	.244	.00691	.154	.308	.692

It was noticed that the residual solutions contained ammonia, and so it was suspected that they might also contain some carbon dioxide. These solutions also gave tests for nitrate ion, showing that some of the ammonia had been oxidized. Since no methods for analyzing and determining ammonia, carbon dioxide, and nitric acid in the presence of ethanol amine were known, it was decided that the investigation would not be continued.

The following table, based upon pure speculation, may possess some significance. From the amount of ammonia

which is missing, that is, the theoretical yield of ammonia less that amount found in runs IIA and B, was calculated the equivalent amount of carbon dioxide which might have been held back in the reaction flasks as ammonium carbonate. This amount of carbon dioxide was added to that already found, and the total yield was compared with the amount of active hydrogen peroxide. According to the equation for complete oxidation to carbon dioxide,

$$NH_2CH_2CH_2OH + 5\ H_2O_2 \longrightarrow 2\ CO_2 + NH_3 + 7\ H_2O,$$

the theoretical ratio of active peroxide to the amount of carbon dioxide formed should be 5/2, or 2.5.

Run	CO_2 (missing) moles	CO_2 found moles	CO_2 total moles	Ratio H_2O_2/CO_2 found	Ratio H_2O_2/CO_2 calc.
IIA	.0805	.155	.2355	2.40	2.50
B	.0800	.244	.3240	2.13	2.50

It must be remembered that this is merely speculation, but if not quite all the carbon dioxide was retained by the ammonia as was calculated, the results might very well be correct. However, it was decided to forego any further investigation on this compound because of the great difficulty encountered in the technical manipulation.

B. Urea

Theoretical

The theoretical discussion of the reaction between urea and hydrogen peroxide is necessarily limited. There is the possibility that hydrogen peroxide may catalyze the hydrolysis of urea to ammonium carbonate. It may also react with the nitrogen in the molecule to yield any or several of the many oxidation products of ammonia. Actually it was found that almost all of the hydrogen peroxide decomposed according to the well-known equation,

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2, \qquad (z)$$

and consequently did not oxidize the urea.

Apparatus and Procedure

The apparatus for this investigation was exactly the same as that employed for the study of ethanol amine, and calls for no further description.

One sixth of a mole of C.P. urea was weighed into each reaction flask, and one and one-half moles of peroxide were added, after the system was swept out with nitrogen. When the water bath reached 65° C., gas was evolved copiously but not violently. When the evolution of gas had ceased the system was again swept out with nitrogen.

Very small increases in weight in the Ascarite towers indicated small yields of carbon dioxide. The amounts of ammonia found in the Millikans were also small. The oxy-

gen was as usual determined by the Hempel method.

The results recorded in Table II are those of one set of runs. It was not deemed adviseable to repeat any work on this compound, since there appeared to be no pronounced oxidation reaction.

Table II

Run	Urea used moles	H_2O_2 used moles	CO_2 found moles	NH_3 found moles	$O_2 \rightleftharpoons H_2O_2$ found moles	H_2O_2 moles	H_2O_2 active moles
A	.167	1.500	.0239	.0209	.742	1.484	.016
B	.167	1.500	.0088	.0064	.745	1.490	.010

Apparantly there is no oxidation of any kind by peroxide, and only a small amount of hydrolysis. This is to be expected in view of the stability of the complex addition compound formed when urea and hydrogen peroxide are mixed.

C. Acetonitrile

Theoretical

The first action to be expected is that described by Radziszewski [8] and Oliveri-Mandala [10], which is hydrolysis to the amide or to the ammonium salt:

$$CH_3CN + H_2O \longrightarrow CH_3CONH_2$$

$$CH_3CONH_2 + H_2O \longrightarrow CH_3COOH + NH_3.$$

The acetic acid may then be oxidized, as described by Payne [2];

$$CH_3COOH + 2\ H_2O_2 \longrightarrow 2\ HCOOH + 2\ H_2O, \qquad (a)$$

$$CH_3COOH + 4\ H_2O_2 \longrightarrow 2\ CO_2 + 6\ H_2O. \qquad (b)$$

The ammonia formed by hydrolysis may also be attacked, as is described by Weith and Weber [16]:

$$2\ NH_3 + 3\ H_2O_2 \longrightarrow N_2 + 6\ H_2O. \qquad (c)$$

The summation of the first two hydrolysis equations gives the one equation:

$$CH_3CN + 2\ H_2O \longrightarrow CH_3COOH + NH_3. \qquad (d)$$

Apparatus and Procedure

The only modification in the apparatus as previously described was the addition of 60-cc. dropping funnels at the tops of the condensers. These were added because it was found that during the run a great deal of ammonium carbonate collected in the lower parts of the condensers, and the only way to remove and decompose it was to allow about twenty-five cc. of six normal sulfuric acid to run down the condensers. The acid dissolved the ammonium carbonate completely, and liberated all of the carbon dioxide. Whatever carbon dioxide was retained in the solutions in the reaction flasks was also expelled by this procedure.

Eastman's pure acetonitrile was fractionated, and only that portion boiling between 80° and 81° C. was collected. Its density was determined, enabling it to be measured instead of weighed. One ninth of a mole was measured into each flask, and somewhat less than one mole of peroxide was added. The necks were then washed down with a few cc. of

distilled water. Since nitrogen was liberated as a product of the reaction, oxygen was used for sweeping out all the apparatus. The water bath was brought gradually to boiling, and after complete evolution of gas the system was swept out with a measured amount of pure oxygen. It was necessary to measure the oxygen added, because some of the peroxide decomposed to give oxygen, and the amount of peroxide unused had to be calculated from the amount of oxygen formed. In the calculations the amount of oxygen used for sweeping out the system was subtracted from that found by gas analysis, and the remainder was used to calculate the amount of peroxide which had decomposed. This procedure was less accurate than the other method, but it was necessary to know how much nitrogen was formed, and since the amount of nitrogen formed was less than a half liter it would have been much more inaccurate to use a measured amount of nitrogen to sweep out the system.

On analysis the gas was found to be almost all oxygen; there was no combustible fraction. The purity of the oxygen used for sweeping out the system was greater than 99.5%, so that the nitrogen found could not be attributed to the impurities in the oxygen.

The carbon dioxide was as usual weighed in the Ascarite towers. Formic acid was determined in the residual solutions by the well-known calomel method [19]. In this method 50-cc. aliquots were taken from the solution which had been made up to 250 cc.. The aliquots were neutralized

with sodium hydroxide in 400-cc. beakers, and diluted to 150 cc.. Then 10 cc. of 50% sodium acetate solution were added, 2 cc. of 10% hydrochloric acid, and finally 25 cc. of mercuric acid reagent, which was prepared by dissolving 100 grams of mercuric chloride and 150 grams of sodium chloride in one liter of water. The beakers were then covered with watch-glasses and heated for two hours suspended in a boiling water bath. At the end of this time all the formic acid had quantitatively reduced the mercuric chloride to insoluble mercurous chloride according to the equation:

$$HCOOH + 2\ HgCl_2 \longrightarrow 2\ HgCl + 2\ HCl + CO_2.$$

The calomel was filtered on asbestos in a Gooch crucible, washed with hot water, alcohol, and finally ether. The crucibles were then dried to constant weight at 105° C. and weighed. From the above equation it was easy to calculate the amount of formic acid originally present.

As before, the ammonia was determined by the difference in acidity of the solution in the Millikan. In this case, however, because some of the ammonia had remained in the reaction flasks combined with the sulfuric acid which had been added, it was necessary to distill aliquots of these solutions with excess alkali, exactly as is done in the Kjeldahl determination of nitrogen, and to titrate the acid in the receiver with standard sodium hydroxide. The amount of ammonia found in these solutions was added to that found in the Millikans.

The acetic acid in the reaction flasks was deter-

mined according to the method of Sherman for the analysis of calcium acetate [20]. The solution was acidified with 25 cc. of pure phosphoric acid and distilled. Water was dropped into the still as fast as the distillate came over, and this was continued until all acid had been removed. The distillate was then titrated with standard sodium hydroxide to determine the amount of acetic acid. Since formic acid is also volatile in steam, it was necessary to subtract the amount of formic acid found by the calomel method from the amount of acid found by the Sherman method in order to obtain the actual amount of acetic acid.

Data

In Table III are presented the yields of all the products of the reaction.

Table IV records the yield of formic acid according to equation (a), the percentage yield, and the amounts of acetonitrile and peroxide required by the equation.

Table V records the yield of carbon dioxide, and the percentage yield according to equation (b), and the amounts of nitrile and peroxide required to form this amount of carbon dioxide.

Table VI contains the yield of nitrogen, and the percentage yield and the peroxide required as calculated from equation (c).

Table VII records the amounts of peroxide required as from equations (a), (b), and (c), their sum, and the amount of active peroxide calculated from equation (z).

Table VIII contains the amounts of acetic acid formed, the nitrile necessary from equation (d), the amounts of nitrile required by equations (a) and (b), and the total amount of nitrile accounted for.

Table IX records the yields of nitrogen and ammonia, the amounts of nitrile necessary according to equations (c) and (d), and the amount of nitrogen accounted for.

For reference purposes the equations to be used are here repeated.

$$CH_3CN + 2\ H_2O \longrightarrow CH_3COOH + NH_3 \qquad (d)$$

$$CH_3COOH + 2\ H_2O_2 \longrightarrow 2\ HCOOH + 2\ H_2O \qquad (a)$$

$$CH_3COOH + 4\ H_2O_2 \longrightarrow 2\ CO_2 + 6\ H_2O \qquad (b)$$

$$2\ NH_3 + 3\ H_2O_2 \longrightarrow N_2 + 6\ H_2O \qquad (c)$$

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 \qquad (z)$$

Table III

Run	CH_3CN used moles	H_2O_2 used moles	NH_3 found moles	CH_3COOH found moles	O_2 found moles	HCOOH found moles	CO_2 found moles	N_2 found moles
A	.111	.915	.0605	.0432	.3745	.00133	.0625	.0183
B	.111	.915	.0613	.0511	.386	.00132	.0584	.0196

Table IV

Run	HCOOH found moles	HCOOH Calc. eq.(a) moles	% HCOOH eq.(a)	H_2O_2 eq.(a) moles	CH_3CN eq.(a) moles
A	.00133	.2222	0.60	.00133	.00067
B	.00132	.2222	0.59	.00132	.00066

Table V

Run	CO_2 found moles	CO_2 calc.eq.(b) moles	% CO_2 eq.(b)	H_2O_2 eq.(b) moles	CH_3CN eq.(b) moles
A	.0625	.2222	28.1	.125	.0312
B	.0584	12222	26.3	.117	.0297

Table VI

Run	N_2 found moles	N_2 calc.eq.(c) moles	% N_2 eq.(c)	H_2O_2 eq.(c) moles	NH_3 eq.(c) moles
A	.0183	.0556	32.9	.0274	.0366
B	.0196	10556	35.3	.0294	.0392

Table VII

Run	H_2O_2 eq.(a) moles	H_2O_2 eq.(b) moles	H_2O_2 eq.(c) moles	H_2O_2 (a)+(b)+(c) moles	H_2O_2 eq.(z) moles
A	.00133	.125	.0274	.1537	.1667
B	.00132	.117	.0294	.1477	.1434

Table VIII

Run	CH_3COOH found moles	$CH_3CN \Rightarrow CH_3COOH$ eq.(d) moles	$CH_3CN \Rightarrow HCOOH$ eq.(a) moles	$CH_3CN \Rightarrow CO_2$ eq.(b) moles	CH_3CN (a)+(b)+(d) moles	% CH_3CN found
A	.0432	.0432	.00067	.0312	.0751	67.6
B	.0511	.0511	.00066	.0297	.0815	73.4

Table IX

Run	NH_3 found moles	$NH_3 \rightleftharpoons N_2$ eq.(c) moles	NH_3 total moles	NH_3 theory moles	% NH_3
A	.0605	.0366	.0971	.1111	87.4
B	.0613	.0392	.1005	.1111	90.5

The discrepancies between the amounts of oxidation products (Table III) and the amounts of peroxide used (Table VII) are surprisingly small, considering the inaccuracy in measuring such small quantities of nitrogen by difference; in run A the total volume of nitrogen was .41 liters, while in B it was .44 liters. The percentage error in measuring the gas volumes was quite appreciable, because the bottles were graduated only in half liters, and the best that could done was to estimate to the nearest five-hundredths of a liter.

The greatest discrepancy is that between the amounts of acetonitrile accounted for by acetic, formic, and carbonic acids (Table VIII), as compared to the amounts of acetonitrile accounted for by the ammonia and nitrogen yields (Table IX). The former amounted to about seventy per cent of the initial nitrile, while the latter amounted to almost ninety per cent. This may possibly be explained by considering the difficulty determining acetic acid accurately enough. It is a well-known fact that the phosphoric acid method at best gives rather low results. If some of the acetic acid were not recovered by this analysis, the difference would be large enough to bring about better checks.

It was assumed that all the nitrile did not react. Only 90% of it was accounted for, and practically all of the peroxide. It may be that the remainder of the nitrile was volatilized during the run, especially while the gas was sweeping out the system; or perhaps it merely remained inert in the solution. If this was the case, one might discount somewhat the amount of ammonia found in the residual solutions, as long boiling with alkali would be sure to hydrolyze some of the nitrile, and thus increase the yield of ammonia. However, if this is the case, the amounts of acetic acid found should also have increased.

A run was made on acetonitrile with addition of enough sulfuric acid to combine with the ammonia as soon as it was liberated by hyrolysis. For this purpose the density of ordinary six normal sulfuric acid was determined in a pyknometer, and the percentage composition was calculated.

One ninth of a mole of acetonitrile, one eighteenth of a mole of sulfuric acid, and one mole of hydrogen peroxide were measured into each reaction flask. Because of the acid in the reaction flask it was unnecessary to use the Millikan wash-bottles. Oxygen was again used to sweep out the system.

The presence of the sulfuric acid caused a much slower evolution of gas. The heating had to be continued for 52 hours before all gases had been liberated. A measured amount of oxygen was again used for removing all residual gases from the system.

Again there was found some gas which was neither

oxygen nor a combustible component, showing that the reaction had again followed equation (c).

The solutions in the reaction flasks were made up to 500 cc., and aliquots were taken for analysis for formic acid. For some unknown reason the results of the calomel method could not be made th check very well, but as the amounts of formic acid were very small, nthing further was done.

Data

The initial amounts of reagents and the yields of formic and carbonic acids, oxygen and nitrogen are recorded in Table X.

Table XI includes observed and calculated yields of formic acid; percentage yields, peroxide and nitrile required according to equation (a).

Table XII contains the same data for carbon dioxide, as calculated from equation (b).

Table XIII contains the same data for nitrogen, as calculated from equation (c).

Table XIV records the amounts of peroxide required as calculated from the yields by equations (a), (b), and (c), their total, and the active peroxide as calculated from the initial peroxide and equation (z).

The equations which are referred to in the tables will be repeated here for convenience.

$$CH_3CN + 2\ H_2O \longrightarrow CH_3COOH + NH_3 \qquad (d)$$

$$CH_3COOH + 2\ H_2O_2 \longrightarrow 2\ HCOOH + 2\ H_2O \qquad (a)$$

$$CH_3COOH + 4\ H_2O_2 \longrightarrow 2\ CO_2 + 6\ H_2O \qquad (b)$$

$$2\ NH_3 + 3\ H_2O_2 \longrightarrow N_2 + 6\ H_2O \qquad (c)$$

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 \qquad (z)$$

Table X

Run	CH_3CN used moles	H_2O_2 used moles	O_2 found moles	N_2 found moles	CO_2 found moles	HCOOH found moles
A	.111	1.000	.397	.0312	.0708	.00205
B	.111	1.000	.395	.0295	.0728	.00299

Table XI

Run	HCOOH found moles	HCOOH calc.eq.(a) moles	% HCOOH eq.(a)	H_2O_2 eq.(a) moles	CH_3CN eq.(a) moles
A	.00205	.2222	0.92	.00205	.00102
B	.00299	.2222	1.34	.00299	.00150

Table XII

Run	CO_2 found moles	CO_2 calc.eq(b) moles	% CO_2 eq.(b)	H_2O_2 eq.(b) moles	CH_3CN eq.(b) moles
A	.0708	.2222	31.9	.1416	.0354
B	10728	.2222	32.8	.1456	.0364

Table XIII

Run	N_2 found moles	N_2 calc.eq.(c) moles	% N_2 eq.(c)	H_2O_2 eq.(c) moles	CH_3CN eq.(c) moles
A	.0312	.0556	56.1	.0468	.0624
B	.0295	.0556	53.1	.0443	.0590

Table XIV

Run	H_2O_2 eq.(a) moles	H_2O_2 eq.(b) moles	H_2O_2 eq.(c) moles	H_2O_2 (a)+(b)+(c) moles	H_2O_2 eq.(z) moles
A	.00205	.1416	.0468	.1905	.206
B	.00299	.1456	.0443	.1929	.210

As in the case of acetonitrile in neutral solution, the original compound is oxidized to carbon dioxide to the extent of a little over 30%. The occurrence of formic acid is very limited, probably because the excess peroxide oxidizes it immediately to carbon dioxide. The ammonia formed by hydrolysis of the nitrile is oxidized to nitrogen to the extent of over 50%. This is greater than the extent of the reaction in neutral solution.

In conclusion it may be stated that in neutral solution at least 70% of the nitrile is hydrolyzed to ammonium acetate, and about 27% is oxidized to carbonic acid, while in acid solution, strong enough to retain all ammonia formed, at least 50% of the nitrile is hydrolyzed, while over 30% of it is oxidized to carbonic acid. In both cases the oxidation goes past the stage of formic acid, as is appar-

ent from the very small yields of this substance. In both runs it was found that ammonia was oxidized, presumably by the intermediate formation and decomposition of ammonium nitrite, to nitrogen, about 35-40% in the neutral solution, and over 50% in the acid solution. This may be because the ammonia was retained better in the acid solution, thus giving a better chance to react.

D. Nitromethane

Theoretical

In the case of the last compound studied it was noted that some of the ammonia was oxidized (perhydrolysis) to ammonium nitrite. Because of this phenomenon the next compound chosen was one in which the nitrogen was already as completely oxidized as possible. The simplest compound of this character is nitromethane.

There are no reports of any work done on the interaction of nitromethane with hydrogen peroxide. The only obvious reaction would be the oxidation of the carbon atom, effected by perhydrolysis of the nitromethane to give methyl alcohol and nitric acid, thus:

$$CH_3NO_2 + H_2O_2 \longrightarrow CH_3OH + HONO_2.$$

If this reaction occurs there will immediately be further oxidation of the methyl alcohol, and it should be in accord with the work of Fry and Payne [2], whose reactions will be set down here without further explanation.

$$CH_3OH + H_2O_2 \longrightarrow HCHO + 2\ H_2O$$
$$2\ HCHO + H_2O_2 \longrightarrow 2\ HCOOH + H_2$$
$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$
$$HCOOH + H_2O_2 \longrightarrow CO_2 + 2\ H_2O$$

It will be shown later that since none of the above-mentioned reaction products was identified there is apparently no reaction between nitromethane and hydrogen peroxide.

Apparatus and Procedure

The same apparatus was used except that the Millikan wash-bottles were omitted because no ammonia was anticipated. The connection from the condenser led directly to the U-tube filled with calcium chloride which was connected to the two Ascarite towers in series.

The nitromethane was prepared by the method described in "Organic Syntheses", as modified in this laboratory by Treon [21]. The method consists of neutralizing chloracetic acid with sodium bicarbonate, heating the solution to 80° C., and dropping in a solution of sodium nitrite as fast as the distillate comes over. When all the nitrite has been added the temperature is raised to boiling, and the remaining nitromethane is distilled over. The product is separated from the water in the distillate, washed with water, and dried over calcium chloride. It is then distilled, the fraction boiling between 100° and 101° C. being reserved.

One fifth of a mole of nitromethane was measured into each reaction flask and one mole of hydrogen peroxide

was added. The system having previously been swept out with nitrogen, the water bath was heated gradually to boiling. The evolution of gas took place very slowly, so that the heating had to be continued for 24 hours before all gas had been completely evolved. The system was then again swept out with nitrogen.

After completion of the run the solutions in the reaction flasks were made up to 500 cc., the gas was measured and analyzed, and the Ascarite towers were weighed. A peculiar phenomenon was observed when weighing the Ascarite towers. In all previous runs the second tower in the series remained at practically constant weight, showing that the absorption was as good as could be expected. However, in this case both towers gained approximately the same weight, near 0.3 grams. Since it is inconceivable that carbon dioxide should behave in this manner, the effect must be attributed to some other cause. It may be that small amounts of nitromethane were volatilized during the run, and that they were absorbed by the Ascarite. As nitromethane is known to form a sodium salt in concentrated aqueous solution, this is probably the explanation of the phenomenon. It is therefore concluded that there was no appreciable amount of carbon dioxide formed during the run.

The gas analyzed as a mixture of oxygen and nitrogen only. The calculation of the amount of active peroxide in one run showed that practically all of the peroxide decomposed to yield oxygen. In the other case the amount of

active peroxide calculated to be somewhat more, but there was s slight leak in the absorption train, which would explain this difference. It was not considered necessary to repeat this work, in view of the fact that there was little if any reaction.

The solutions from the reaction flasks were slightly brownish in color, and were not examined further.

Data

Table XV presents the amounts of nitromethane and peroxide used at the start, and the amounts of oxygen and active peroxide.

Table XV

Run	CH_3NO_2 used moles	H_2O_2 used moles	O_2 found moles	H_2O_2 moles	active H_2O_2 moles
A	.2000	1.000	.463	.926	.074
B	.2000	1.000	.329*	.658	.342*

It is evident from the figures for sample A that there is very little reaction between nitromethane and hydrogen peroxide. Most of the peroxide decomposes to yield oxygen.

* Leaked during the run.

E. Glycine

Theoretical

The first step in the reaction of glycine is probably deamination to form glycollic acid and ammonia.

$$NH_2CH_2COOH + H_2O \longrightarrow CH_2OH\text{-}COOH + NH_3 \qquad (e)$$

The glycollic acid so formed should then reacty in exactly the same manner as it did in the investigation of Milstead [3]. As has been stated in the historical section he showed that the following reactions took place:

$$CH_2OH\text{-}COOH + 2\ H_2O_2 \longrightarrow 3\ H_2O + CO_2 + HCOOH \qquad (f)$$

$$2\ CH_2OH\text{-}COOH + 2\ H_2O_2 \longrightarrow 4\ H_2O + 2\ CO_2 + 2\ HCOOH + H_2 \qquad (g)$$

$$HCOOH + H_2O_2 \longrightarrow 2\ H_2O + CO_2. \qquad (h)$$

It would probably be possible to stop at the stage of glyoxylic acid, provided the oxidizing agent be weak enough, but Milstead found no glyoxylic acid, and since, in this investigation, as excess of hydrogen peroxide was used, there should be no glyoxylic acid in the solutions after the run.

Apparatus and Procedure

The apparatus used in this work was the same as that described under the section on acetonitrile. The gas used for sweeping out the system was nitrogen.

One eighth of a mole of glycine, Eastman (ammonia-free), M.P.230-236° dec., was weighed into each flask, and one mole of peroxide was added. The bath was as usual brought gradually to the boiling point, and after complete

evolution of gas the system was swept out with nitrogen.

The gas collected in the gasometers proved to be only oxygen and nitrogen. No hydrogen was found, thus excluding the possibility of reaction (g). Only small amounts of carbon dioxide were found, and no formic acid was found in the solutions from the reaction flasks, thus necessitating a summation of equations (f) and (h), to give equation (i):

$$CH_2OH\text{-}COOH + 3\ H_2O_2 \longrightarrow 2\ CO_2 + 5\ H_2O. \qquad (i)$$

Data

Table XVI contains the initial amounts of reagents, and the yields of carbon dioxide and oxygen.

Table XVII records the amounts of carbon dioxide, the amounts of peroxide required for their formation according to equation (i), and the active peroxide as calculated from the yields of oxygen and the initial peroxide.

For convenience in reference the necessary equations are here repeated.

$$NH_2CH_2COOH + H_2O \longrightarrow CH_2OH\text{-}COOH + NH_3 \qquad (e)$$

$$CH_2OH\text{-}COOH + 3\ H_2O_2 \longrightarrow 2\ CO_2 + 5\ H_2O \qquad (i)$$

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 \qquad (z)$$

Table XVI

Run	Glycine used moles	H_2O_2 used moles	O_2 found moles	CO_2 found moles
A				
A	.125	1.000	.449	.0094
B	.125	1.000	.442	.0132

Table XVII

Run	CO_2 found moles	H_2O_2 eq.(i) moles	H_2O_2 eq.(z) moles	active H_2O_2 moles	H_2O_2 unaccounted for, moles
A	.0094	.0143	.898	.102	10877
B	.0132	.0198	.884	.116	.1062

It will be seen that most of the active hydrogen peroxide remains unaccounted for by the above equation (i). No further work was done on this compound because of the slight extent of oxidation to carbon dioxide.

F. Hydrogen Cyanide

Theoretical

Hydrogen peroxide in the presence of hydrogen peroxide may undergo both hydrolysis and perhydrolysis, the former yielding ammonia and formic acid, and the latter producing ammonia and carbonic acid.

$$HCN + 2\,H_2O \longrightarrow HCOOH + NH_3 \qquad (j)$$

The formic acid may be oxidized to carbonic acid, thus:

$$HCOOH + H_2O_2 \longrightarrow CO_2 + 2\,H_2O. \qquad (k)$$

Equations (j) and (k) may be summed up in the one equation:

$$HCN + H_2O_2 \longrightarrow CO_2 + NH_3. \qquad (l)$$

The formation of oxamide may be represented as follows:

$$2\ HCN + H_2O_2 \longrightarrow (CN)_2 + 2\ H_2O$$

$$(CN)_2 + 2\ H_2O \longrightarrow (CONH_2)_2.$$

and by adding these two equations;

$$2\ HCN + H_2O_2 \longrightarrow (CONH_2)_2. \qquad (m)$$

Equation (m) may be disregarded because oxamide was found only in one run, and it was impossible to determine the quantity of it in this case.

Apparatus and Procedure

Since hydrogen cyanide boils at 25° C. it may be expected to volatilize and pass through the condensers into the absorption train with the other gaseous products. It is necessary to know just how much of the initial hydrogen cyanide has thus escaped reaction, in order to calculate the amount which has been attacked by the peroxide.

For this purpose a modified absorption train was developed. The Millikan wash-bottles contained 100 cc. each of normal nitric acid and normal silver nitrate. The nitric acid was used for absorbing ammonia, and the silver nitrate was used to absorb the hydrogen cyanide. The amounts of these two solutions were calculated to be slightly in excess of the total possible yields of ammonia and hydrogen cyanide.

Ammonia was determined by the difference in the acidity of the solutions before and after the run. If much

cyanide was volatilized, a correction had to be applied. The cyanide reacts as follows:

$$HCN + AgNO_3 \longrightarrow HNO_3 + AgCN.$$

For every molecule of silver cyanide formed, one molecule of nitric acid would also be formed. The amount of nitric acid formed in this way had to be subtracted from the amount found in the solution after the run. The remainder was then subtracted from the initial amount of nitric acid. The final remainder was then equal to the amount of ammonia absorbed.

The solutions were also titrated before and after the run with tenth-normal potassium thiocyanate, with ferric alum as indicator. The difference in the amounts of silver nitrate before and after the run was equal to the amount of hydrogen cyanide volatilized.

It was found by experiment that the tips of the tubes in the Millikan wash-bottles became clogged very easily. This was because of the formation of only a small amount of silver cyanide, which was a quite voluminous precipitate. A modification was made by placing an ordinary gas wash-bottle immediately preceding the Millikan wash-bottle in each train. Most of the nitric acid and a small amount of the silver nitrate solutions were placed in this first bottle, while the remaining nitric acid and silver nitrate were placed in the Millikan. All silver cyanide was formed in the first bottle, and the second served merely as a check. The precipitate was formed in the comparatively large tube in the first wash-bottle, and it would usually

become dislodged and fall to the bottom. Most of the acid was placed in the first wash-bottle in order to insure that the solution would always remain acid, so that it would not absorb any carbon dioxide.

One additional Millikan wash-bottle was placed in each train in place of the Ascarite towers and accompanying drying tubes. These Millikans contained 200 cc. of approximately normal sodium hydroxide, which was designed to absorb all the carbon dioxide liberated. The carbon dioxide content of the sodium hydroxide was determined before and after the run by titrating portions of the solution with standard acid, using methyl orange as indicator. Other portions were titrated very slowly with standard acid and phenolphthalein in the presence of excess barium chloride. The barium chloride reacted with any carbonate present to form insoluble barium carbonate, which was not affected by the acid provided the titration was carried out slowly.

The titration with methyl orange gave the total alkali, both free and combined, while the titration with phenolphthalein and barium chloride gave only the free alkali. The difference between these two values was equal to the amount of carbonate in the solution.

The Millikan wash-bottles were substituted for the Ascarite towers because it was feared that some nitric acid might volatilize, and therefore would be weighed as carbon dioxide. With this modification small amounts of acid would not cause any error, because the difference between the

free and total alkali was determined, not the alkalinity.

By making several preliminary runs it was found that this method of absorbing carbon dioxide was unreliable, because some of the carbon dioxide escaped absorption. Much better results were obtained from the Ascarite towers and their accompanying drying tubes.

The hydrogen cyanide was prepared from powdered potassium cyanide, C.P.. The potassium cyanide was placed in a 500-cc. flask, and a two-hole stopper carrying a dropping funnel and an outlet tube was inserted. The outlet tube led to an inverted funnel in a beaker of distilled water, which was set in crushed ice. Sulfuric acid, one part of acid to one of water, was dropped onto the cyanide. The gaseous hydrogen cyanide was liberated very copiously, and was absorbed in the beaker of water. It was found adviseable to place a U-tube filled with dry glass beads in the tube leading to the absorption vessel. This U-tube was suspended in a beaker of water maintained at not more than 40° C., and served as an excellent fractionating column for removing higher-boiling polymers of hydrogen cyanide. It was found impossible to keep the solutions of hydrogen cyanide for much more than a day, so they were prepared as needed.

The strength of the hydrogen cyanide solution was determined according to Liebig's method, as described by Treadwell-Hall [22]. Ten cc. of the solution were pipetted into a 100-cc. volumetric flask and made up to volume. Ten-cc. aliquots of this diluted solution were titrated in

excess potassium hydroxide by tenth-normal silver nitrate. A small amount of potassium iodide was added to sharpen the end-point. The desired amount of hydrogen cyanide solution could be run into the reaction flasks from a measuring pipette.

Nitrogen was used to sweep out all residual gases, and one tenth of a mole of hydrogen cyanide was placed in the reaction flasks. The proper amount of peroxide was run in, the solution made up to the desired volume, and the apparatus was connected. All the runs made on hydrogen cyanide were allowed to stand at least sixteen hours before being heated. The one in which excess cyanide was used was allowed to stand two days before heating. After heating and complete evolution of gas, 25 cc. of six normal sulfuric acid were placed in each dropping funnel, and allowed to run down the condensers, removing and reacting with the ammonium carbonate. The system was then swept out with nitrogen.

Runs were made using one tenth of a mole of hydrogen cyanide, and one mole, one tenth of a mole, and one twentieth of a mole of hydrogen peroxide, respectively, in 125 cc. of solution. The run with excess hydrogen peroxide gave the same results as the one in which the peroxide was in the same molar concentration as the cyanide, so it will not be discussed. It was necessary to use a definite volume of solution because it was impossible to prepare the hydrogen cyanide in the same concentration for each run. Another run was made using one tenth of a mole each of cyanide and per-

oxide in 250 cc. of solution; i.e., just half the concentration of the other runs. The amounts will be referred to in the tables as one twentieth of a mole each, and the results will be calculated on this basis, considering these amounts as having been in 125 cc. of solution.

Data

Table XVIII records the amounts of peroxide and cyanide used, the yields of carbon dioxide, ammonia, formic acid and oxygen.

Table XIX contains the yields of carbon dioxide, the theoretical yields according to equation (l), the percentage yields, the amounts of peroxide required by the equation, and the active peroxide, or the initial peroxide less that equivalent to the oxygen, equation (z).

Table XX contains the yields of formic acid, the amounts of cyanide required by the equation (j), the amounts of cyanide required by equation (l), the amounts of cyanide recovered unreacted, and the total amounts of cyanide accounted for.

Table XXI contains the yields of ammonia and the yields of ammonia calculated according to equations (j) and (l).

The two equations required for these calculations are here repeated.

$$HCN + 2\ H_2O \longrightarrow HCOOH + NH_3 \qquad (j)$$

$$HCN + H_2O_2 \longrightarrow CO_2 + NH_3 \qquad (l)$$

Table XVIII

Run	HCN used moles	H_2O_2 used moles	NH_3 found moles	HCOOH found moles	CO_2 found moles	O_2 found moles	HCN unreacted moles
IA	.100	.100	.0914	.00575	.0865	..0056	.00126
B	.100	.100	.0882	.00597	.0827	.0068	trace
IIA	.100	.050	---	---	.0286	.0110	.0448
B	.100	.050	---	---	.0364	.0094	.0422
IIIA	.050	.050	.0470	.00431	.0404	.0032	trace
B	.050	.050	.0455	.00429	.0404	.0031	trace

Table XIX

Run	CO_2 found moles	CO_2 eq.(I) moles (calc)	% CO_2 eq.(I)	H_2O_2 eq.(I) moles (calc)	H_2O_2 eq.(z) moles	H_2O_2 active moles	% H_2O_2 accounted for
IA	.0865	.1000	86.5	.0865	.00112	.0888	97.4
B	.0827	.1000	82.7	.0827	.00136	.0864	95.8
IIA	.0286	.0500	57.2	.0286	.0220	.0280	102.0
B	.0364	.0500	72.8	.0364	.0188	.0312	116.7
IIIA	.0404	.0500	80.8	.0404	.0064	.0436	92.6
B	.0404	.0500	80.8	.0404	.0062	.0438	92.2

Table XX

Run	HCOOH found moles	HCN $\rightleftharpoons$ HCOOH eq.(j) moles	HCN $\rightleftharpoons$ CO_2 eq.(l) moles	HCN unreacted moles	total HCN accounted for moles	% HCN accounted for
IA	.00575	.00575	.0865	.00126	.0935	93.5
B	.00597	.00597	.0827	trace	.0887	88.7
IIA	---	---	.0286	.0448	.0734	73.4
B	---	---	.0364	.0422	.0786	78.6
IIIA	.00431	.00431	.0404	trace	.0447	89.6
B	.00429	.00429	.0404	trace	.0447	89.6

Table XXI

Run	NH_3 found moles	NH_3 ⇒ HCOOH eq.(j) moles	NH_3 ⇒ CO_2 eq.(l) moles	total NH_3 eq.(j)+(l) moles	% NH_3 found
IA	.0914	.00575	.0865	.0924	98.9
B	.0882	.00597	.0827	.0887	99.4
IIA	---	---	.0286	---	---
B	---	---	.0364	---	---
IIIA	.0470	.00431	.0404	00447	105.1
B	.0455	.00429	.0404	.0447	101.8

The amounts of formic acid and ammonia in the residual solutions in run II could not be determined because the excess of hydrogen cyanide had polymerized, yielding a black precipitate in a brown solution. Some crystals of oxamide were observed in these solutions, but the amounts could not be determined because of the interfering polymers. No oxamide was observed in either of the other runs.

It will be seen that 80-90% of the initial hydrogen cyanide was accounted for in runs I and III. What became of the remainder of the cyanide is as yet unknown.

Approximately eighty per cent of the cyanide was oxidized to carbonic acid, which is in agreement with the report of Masson on his work on potassium cyanide, see page 12.

GENERAL SUMMARY AND CONCLUSIONS

The quantitative study of the action of aqueous hydrogen peroxide on simple organic compounds has been extended to simple carbon-nitrogen compounds; Namely, ethanol amine, urea, acetonitrile, nitromethane, glycine, and hydrogen cyanide. In those cases in which extensive reaction occurred the proposed equations were verified by the amounts of products obtained and the quantities of hydrogen peroxide participating in the reactions. The general summary and conclusions are as follows:

A. The action of hydrogen peroxide on ethanol amine in solution at 100° C. gave very inconsistent results, which were attributed to the marked alkalinity of the solution of the amine. Somewhat over fifty per cent of the amine was oxidized to carbonic acid, and considerable quantities of ammonia were formed, showing that the amine was hydrolyzed to glycol, thus:

$$NH_2CH_2CH_2OH + H_2O \longrightarrow CH_2OH\text{-}CH_2OH + NH_3.$$

Tests for nitric acid showed that ammonia was oxidized not only to nitrite,

$$NH_3 + 3\ H_2O_2 \longrightarrow 4\ H_2O + HONO,$$

but also to nitrate, by the action of the peroxide. Effront got the same results in an acid solution.

B. Urea is not oxidized by hydrogen peroxide, and is only hydrolyzed to a small extent. The presence of urea inhibits the decomposition of hydrogen peroxide below 60° C.,

while above this temperature the hydrogen peroxide decomposed according to the equation:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2. \qquad (z)$$

C. Acetonitrile reacted with hydrogen peroxide, yielding practically the same results in either acid or neutral solutions. It was hydrolyzed to ammonia and acetic acid to approximately seventy per cent of theory. The reactions of acetic acid with hydrogen peroxide as studied by Payne [2] also occurred in this case.

$$CH_3COOH + 2\ H_2O_2 \longrightarrow 2\ HCOOH + 2\ H_2O \qquad (a)$$

$$CH_3COOH + 4\ H_2O_2 \longrightarrow 2\ CO_2 + 6\ H_2O. \qquad (b)$$

Reaction (a) occurs to less than one per cent of theory, probably because of the excess peroxide, which would oxidize the formic acid to carbonic acid. Reaction (b) occurs to roughly twenty-five per cent of theory. The oxidation of ammonia to ammonium nitrite, which yields nitrogen, is summarized in the equation

$$2\ NH_3 + 3\ H_2O_2 \longrightarrow N_2 + 6\ H_2O, \qquad (c)$$

which occurs to from thirty to forty per cent of theory.

The perhydrolysis mechanism is thus upheld by the reactions of acetonitrile with hydrogen peroxide, especially by the one in which ammonia is oxidized.

D. Nitromethane remains practically unaffected by hydrogen peroxide, showing that the reactions

$$CH_3NO_2 + H_2O \longrightarrow CH_3OH + HNO_2$$

and

$$CH_3NO_2 + H_2O_2 \longrightarrow CH_3OH + HONO_2$$

do not take place to any appreciable extent.

E. With glycine and hydrogen peroxide less than ten per cent of the initial amount of glycine is oxidized to carbon dioxide, according to the equation

$$NH_2CH_2COOH + 3\ H_2O_2 \longrightarrow 2\ CO_2 + 4\ H_2O + NH_3.$$

The amount of peroxide required for this oxidation is much less than that actually used in the esperiment.

F. Hydrogen cyanide reacts almost completely with hydrogen peroxide when the two reagents are used in the one-to-one ratio required by the equation

$$HCN + H_2O_2 \longrightarrow CO_2 + NH_3. \qquad (1)$$

Approximately eighty per cent of the cyanide is oxidized to carbon dioxide and about six per cent more is hydrolyzed to formic acid. No oxamide is produced. The remainder of the cyanide has not as yet been accounted for.

When the ratio of cyanide to peroxide used was two-to-one, between twenty-eight and thirty-six per cent of the initial cyanide was oxidized to carbon dioxide, and a quantity was oxidized to oxamide. A great deal of the remaining cyanide polymerized in the solution, thus preventing the further examination of the solution after completion of the run.

The equations for all of the reactions which were found to occur were explained in terms of the perhydrolysis mechanism of reaction.

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