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Approved by:

D. Shipley Fry

W. M. Burgess, Chairman

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A REACTION MECHANISM STUDY: THE ACTION OF CONCENTRATED AQUEOUS SODIUM HYDROXIDE SOLUTION UPON ALIPHATIC COMPOUNDS ACCOMPANIED BY THE LIBERATION OF HYDROGEN

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by

John W. Haefele

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M. S. University of Cincinnati 1935

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I

INTRODUCTION

The explanation of the liberation of large amounts of hydrogen gas when many organic compounds react with hot or molten sodium hydroxide readily becomes apparent if the thermal dissociation of caustic alkali is considered.

As water is heated, the dissociation into $\overset{+}{H}$ and $\overset{-}{OH}$ increases rapidly, so that at 100° the value of the dissociation constant is much greater than the value at zero degrees. If sodium hydroxide be regarded as H O H with one hydrogen atom replaced by metal, then on heating, its dissociation, like that of water, ought to increase with rise in temperature. But how would sodium hydroxide dissociate? Since sodium 'has more affinity' for oxygen than has hydrogen, as is shown by the relative magnitudes of the heats of formation of Na_2O and H_2O, it is logical to assume dissociation into $\overset{+}{H}$ and $\overset{-}{ONa}$, because only thus can the sodium retain the oxygen. It may not be claimed, however, that this $\overset{+}{H}$ is a hydrogen ion, it having been amply demonstrated that the ordinary hydrogen <u>ion</u> is in reality the hydrated oxonium ion, $H_3\overset{+}{O}$. Hence this $\overset{+}{H}$ should be distinguished by the term <u>dissociated</u> rather than ionized hydrogen.

Just as with water, as the temperature is raised, the concentration of the dissociated hydrogen from sodium hydroxide increases, becoming finally sufficient to effect the occurrence of many interesting reactions between organic compounds and hot alkali. If in addition to the temperature required to produce dissociation, the alkali is also brought into the liquid state by fusion, so that reaction mixtures will be homogeneous, then quantitative reactions occur that are explicable only on the basis of the dissociation of hydrogen from the fused alkali.

Since the year 1923, Fry and his co-workers have carried out investigations of the action of caustic alkalies in the fused state(1), in methyl alcohol solution as sodium methylate(2), and in aqueous solution(3), upon relatively simple aliphatic compounds, with the view of obtaining quantitative data to prove both the nature and the extent of the occurrence of certain postulated reactions in relation to the mechanism of the oxidations that take place. The equations representing these various reactions were based upon two typical equations, thus:

$$R(H)_n + n\ MOH \rightarrow R(OM)_n + n\ H_2$$

$$R(CH_3)_n + n\ MOH \rightarrow R(OM)_n + n\ CH_4$$

where M is Na or K, and $R(OM)_n$ is either an alkali formate or carbonate.

The underlying hypothesis proposed was the assumption that the caustic alkalies in the fused state undergo acidic dissociation thus:

$$MOH \rightleftharpoons \overset{+}{H} + \overset{-}{OM}.$$

This hydrogen then combines with the hydrogen atoms or methyl groups of the organic compound, thereby liberating gaseous hydrogen or methane while the carbon compound is oxidized, usually yielding, with fused alkali, sodium carbonate; but in methyl alcohol solution, sodium formate; and in aqueous solution, various salts. "When hydrogen is not liberated, the carbon compound suffers both oxidation and reduction concomitantly."(4)

As previously stated, it was found that the mechanism of certain reactions occurring in sodium hydroxide solution could be explained by assuming the acidic dissociation of caustic alkali.

Fry and Cameron (2) proposed the following equations to represent the mechanism of Klinger's reaction, which occurs in methyl alcohol solution:

$$3CH_3ONa + 3H_2O \rightarrow 3CH_3OH + 3HONa \quad (a)$$
$$3CH_3OH + 3HONa \rightarrow 3HCOONa + 12H \quad (b)$$
$$4C_6H_5NO_2 + 12\,H \rightarrow 2(C_6H_5N)_2O + 6\,H_2O \quad (c)$$

$$\Sigma(a,b,c)\ 4C_6H_5NO_2 + 3CH_3ONa \rightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \quad (A)$$

Equation (A), the summation of a, b, and c, was shown to occur to the extent of 88% of the theory for the amount of nitrobenzene taken. The yield of sodium formate agreed quantitatively with the yield of azoxybenzene. It will be noted that equation

b, involving the acidic dissociation of sodium hydroxide, is an example of the general equation

$$R(H)_n + n\ MOH \rightarrow R(OM)_n + n\ H_2.$$

However, in this system, the hydrogen is not liberated, but is used for the reduction of the nitrobenzene.

Fry and Treon (3) developed a complete mechanism for an oxidation-reduction reaction between nitromethane and aqueous sodium hydroxide solution, as follows:

$$CH_3NO_2 + 3HONa \rightarrow C(ONa)_3NO_2 + 6\ H \qquad (d)$$

$$C(ONa)_3NO_2 + 6\ H \rightarrow C(ONa)_3NH_2 + 3H_2O \qquad (e)$$

$$C(ONa)_3NH_2 + HONa \rightarrow C(ONa)_4 + NH_3 \qquad (f)$$

$$C(ONa)_4 + H_2O \rightarrow Na_2CO_3 + 2HONa \qquad (g)$$

$$\sum(d,e,f,g)\quad CH_3NO_2 + 2HONa \rightarrow Na_2CO_3 + NH_3 + H_2O \qquad (B)$$

Here again, equation d exemplifies the general reaction resulting from the acidic dissociation of sodium hydroxide. Equation (B), the summation of d, e, f, and g, was quantitatively verified, and similar reaction schemes were developed and verified for nitrourea, nitroguanidine, and nitrobarbituric acid.

Price and Uber, with Fry (3), showed that the Cannizarro reaction occurs according to the following scheme, wherein the hydrogen formed according to the type reaction (h) participates in the consecutive reduction reaction (i):

$$CH_2O + HONa \rightarrow HCOONa + 2\,H \qquad (h)$$

$$CH_2O + 2\,H \rightarrow CH_3OH \qquad (i)$$

$$\Sigma(h,i)\quad 2CH_2O + HONa \rightarrow HCOONa + CH_3OH \qquad (C)$$

Equation (C), the summation of h and i, represents Cannizarro's reaction.

In the three examples cited above, concomitant oxidation and reduction occur, and hydrogen is not liberated. However, Price and Uber obtained a quantity of gaseous hydrogen when formaldehyde was reacted with aqueous sodium hydroxide; that is, some of the hydrogen represented by equation h was evolved as gas, so that not all of it was used for the reduction according to equation i. Unpublished data of F. E. Miller of this laboratory, to be given below, showed that a quantitative yield of hydrogen could be obtained by the action of a concentrated aqueous solution of sodium hydroxide on sodium formate.

No other previous accounts have been found in the literature which describe quantitative studies of the action of concentrated sodium hydroxide solution upon carbon compounds in relation to the liberation of hydrogen. Accordingly, in the present research it was decided to determine whether simple aliphatic compounds containing carbon, hydrogen, and oxygen, will liberate hydrogen from aqueous alkali as they do from fused alkali; and if so, whether the nature of the reactions and products is in agreement with the type equations proposed above.

The objects of this investigation, then, may be summarized as follows:

1. To study the reactions of carbon compounds with hot concentrated aqueous sodium hydroxide solution, approximately thirty-five normal.

2. To estimate quantitatively the yields of the products formed, in order to substantiate both the occurrence and the extent of the occurrence of the reactions observed.

3. To determine whether or not the equations, derived from the proposed reaction mechanism schemes, are in conformity with the quantitative data obtained in (2).

4. To study the effect of an organic base, notably piperidine, upon the nature and the extent of occurrence of these reactions.

II

GENERAL OBSERVATIONS AND THEORETICAL DISCUSSION

The reaction-mechanism schemes proposed in this study involve the acidic dissociation of sodium hydroxide, and thus regard this notably strong base as an amphoteric compound. It is here pertinent to note, in connection with the conception of amphoterism, that the strong acids, nitric and sulfuric acids, in nitration and sulfonation reactions respectively, react as bases, dissociating to yield hydroxyl radicals in conformity with the following equations:

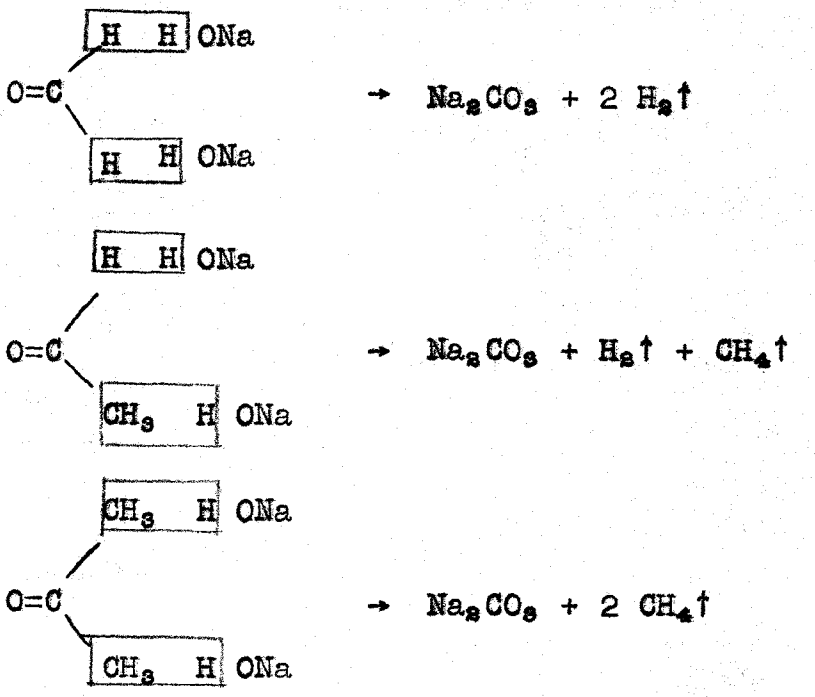
$$C_6H_5.H + HO.NO_2 \rightarrow C_6H_5.NO_2 + H.OH$$

$$C_6H_5.H + HO.SO_2.OH \rightarrow C_6H_5.SO_2.OH + H.OH$$

In logical contrast, the strong bases, such as sodium and potassium hydroxide, in concentrated solution react as acids, dissociating to yield hydrogen radicals in conformity with numerous examples previously cited.

Fry (4) has suggested a rule which has held for all compounds that have so far been reacted with fused alkali, namely that "every hydrogen atom and every methyl radical in union with a carbon atom, which carbon atom is in turn united to an oxygen atom, yields respectively a molecule of hydrogen and a molecule of methane, through its combination with an atom of hydrogen from the anhydrous fused caustic

alkali (4)." This rule, as well as the type reaction mechanism involving the apparent acidic dissociation of sodium hydroxide, is directly illustrated as follows:



In many reactions, particularly those with more complex compounds, the above rule is not directly applicable. These apparent exceptions to the rule, however, are readily explained and correlated with the rule, when the compound is regarded as being transformed, by internal rearrangement or intramolecular oxidation-reduction reactions, into other products, each of which in turn reacts with the caustic alkali in direct conformity with the rule.

For example, a molecule of ethylene glycol yields with fused alkali five molecules of hydrogen, whereas by strict application of the rule only four would be expected.

In this particular case, under the thermal and alkaline conditions of the reaction mixture, "the glycol molecule undergoes an oxidation-reduction change in order to react as one molecule each of formaldehyde and methyl alcohol. The former according to rule has been shown to liberate two, and the latter three, that is, a sum total of five molecules of hydrogen" (4), the number that is actually obtained from glycol. These facts are summarized in the following scheme:

$$CH_2OHCH_2OH \rightleftharpoons CH_2O + CH_3OH \qquad (a)$$

$$CH_2O + 2HONa \rightarrow Na_2CO_3 + 2\,H_2\uparrow \qquad (b)$$

$$CH_3OH + 2HONa \rightarrow Na_2CO_3 + 3\,H_2\uparrow \qquad (c)$$

$$\sum(a,b,c)\quad CH_2OHCH_2OH + 4HONa \rightarrow 2Na_2CO_3 + 5\,H_2\uparrow \qquad (A)$$

When reactions involving caustic alkali occur in solution, hydrogen need not be evolved, for, as amply illustrated by the discussions of the Klinger, Cannizarro, and Nitromethane reactions in the preceding section, concomitant oxidation and reduction may occur.

The reactions of organic compounds in the fused state and in the concentrated aqueous medium are usually similar, in some cases even identical. However, reaction does not occur if the solution of sodium hydroxide is too dilute, indicating that the presence of too much water will favor the normal dissociation into sodium and hydroxyl ions.

Some general differences, of degree rather than kind, were noted when the reactions in the two media were compared. By fused alkali, under proper conditions, most compounds are oxidized to sodium carbonate with the liberation of hydrogen or methane or both. In the aqueous medium the liberation of methane was never observed, and oxidation seldom proceeded to the carbonate stage. Further, many compounds that react with fused alkali do not react in the aqueous medium.

III

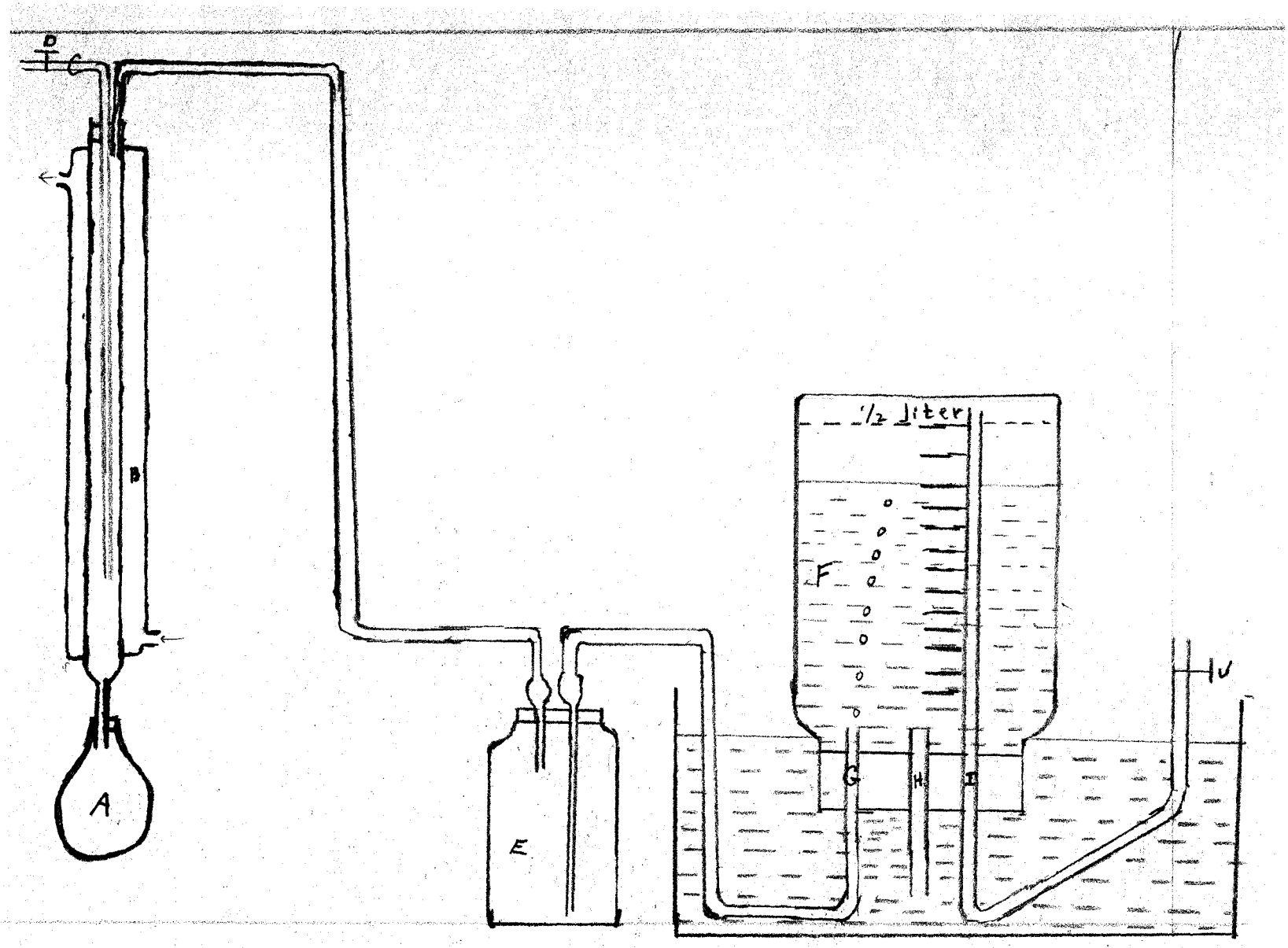
APPARATUS, PROCEDURE, AND ANALYTICAL METHODS

A. Apparatus and Procedure

The purpose of the present investigation was to determine the nature and the extent of the occurrence of the reaction of approximately thirty-five normal aqueous sodium hydroxide solution upon five compounds, namely, sodium formate, formaldehyde, glyoxylic acid, ethylene glycol, and glycerine.

Experimental runs were conducted in duplicate with each compound according to the following general procedure:

The copper reaction-flask A (Fig. 1) of 700 cc capacity was connected to a meter, water-cooled, reflux condenser B by a tightly-fitting rubber stopper. A two-holed rubber stopper was fitted to the top of the inner tube of the condenser. Through one hole was passed a long glass tube C, extending three-fourths of the way down into the condenser, and closed at the end outside the condenser by a glass stop-cock. Through the other hole a bent glass tube led to the gas-washing bottle E, which functioned as a safety-bottle, whence the gas was delivered into a gasometer F—an inverted eight liter carboy, calibrated in half-liters, and fitted with a rubber stopper having three outlets, G, H, and I. Outlet G allowed the delivery of gas



from the safety-bottle E, H permitted the escape of the liquid displaced from the gasometer, while through I passed a long glass tube by means of which samples of gas could be drawn off for analysis. All necessary rubber connections, pressure-tubing of medium weight, were made gas-tight by wiring firmly against the glass tubes over which they fitted.

The operation of a run with this apparatus was accomplished as follows:

After filling the gasometer with concentrated brine to reduce the loss of hydrogen by solution, stop-cock D and screw-clamp J were closed. Flask A was charged with the reaction mixture, connected to the condenser, and heated in an oil-bath until a lively and steady, but not too rapid, stream of hydrogen was obtained. The bath was brought to a constant temperature, which was recorded. The flask was then heated until no further evolution of hydrogen was noted. Tube C was then connected to a compressed air outlet, stop-cock D was opened, and a stream of air was passed through the apparatus to insure that all the evolved hydrogen was finally delivered into the gasometer. The reaction mixture remaining in flask A was cooled and diluted until all soluble material was dissolved, and then was made up to a definite volume of two to four liters. Aliquots of this total volume were taken for analysis of the quantities of

substances formed in the reaction.

By removing the safety-bottle E, sealing the glass tube K, using a rubber tube and a screw-clamp, and then forcing water from the tap into the gasometer through H while the clamp J was open, samples of gas were obtained for analysis of its hydrogen content.

Such quantities of compounds were used in the charges placed in flask A as would give reasonable and convenient volumes of hydrogen in the gasometers. It was, of course, often necessary to make a preliminary run to get some idea of the volume of hydrogen to be expected from the reaction of the particular compound under examination.

It was also necessary to do some preliminary work to determine the concentration of alkali solution that would be required to effect reaction. Towards this end, F. E. Miller, in 1931, had, in this laboratory, treated sodium formate with hot solutions of sodium hydroxide, and in successive runs increased the amount of alkali by constant increments until a quantitative evolution of hydrogen was obtained. Miller's unpublished data is found in the following table:

ACTION OF AQUEOUS ALKALI ON HCOONa

Table of Mr. Fred E. Miller
Experiments, October, 1931

Run	Total vol. (cc)	Cu turn-ings?	Heat-ing time (hrs.)	Wgt. HCOONa (grams)	Wgt. HONa (grams)	Total gases (cc)	B. P. °C.	Volume H_2 S.T.P. theory 5600 cc
1	250	yes	2.0	17	100	400	124	N.F.
2	"	no	2.0	"	150	275	141	N.F.
3	"	yes	3.5	"	200	400	150	N.F.
4	"	"	2.5	"	250	480	167	N.F.
5	"	"	4.5	"	300	480	193	N.F.
6	"	"	6.0	"	350	6250	217	5500

Notes:

1. N.F. = "none found"
2. Probable expansion of air in apparatus, 500 cc
3. Qualitative test for carbonate: positive
4. Qualitative test for oxalate: trace only

Miller's data shows that the concentration of sodium hydroxide solution in run six, 350 grams of alkali per 250 cc of solution, approximately 35 normal, effected practically theoretically complete reaction.

A supplementary test showed that if 350 grams of sodium hydroxide and 88 cc of water were mixed and heated, then the volume of the resulting solution was about 250 cc, so that this concentration corresponded to Miller's run six. This mixture yields a clear solution when heated. Under a reflux condenser, water begins to form a condensation-collar at 225°, and refluxing is vigorous at 250°. This solution-mixture solidifies when cooled, but melts again at 190-200°. This standard concentration of alkali, about 35 normal, was used in all runs.

B. Analytical Methods

This section describes the analytical methods employed to determine the yields of the various products of reaction obtained when the five compounds investigated, namely, sodium formate, formaldehyde, glyoxylic acid, ethylene glycol, and glycerine, interacted with thirty-five normal sodium hydroxide solution.

It was necessary to determine the yields of a number of products, which are listed below in the order in which the analytical procedures are described; the

list also indicates the compounds from which each reaction-product was obtained:

REACTION PRODUCT	SOURCE
a. Hydrogen	Sodium formate, formaldehyde, glyoxylic acid, glycol, glycerine.
b. Sodium carbonate	Sodium formate, formaldehyde, glycerine.
c. Sodium formate (residual)	Sodium formate.
d. Sodium glycollate	Glycol, glyoxylic acid.
Ethylene glycol (residual)	Glycol.
e. Sodium oxalate and sodium glycollate.	Glyoxylic acid.
f. Sodium lactate	Glycerine.
Glycerine (residual)	Glycerine.

The method of sampling gas from the gasometer for the determination of hydrogen, has been described above. Sampling in every other determination was accomplished by pipetting aliquots of the reaction mixture, which had previously been dissolved and diluted to a definite volume. If the quantity of material found in the aliquot was g, then the quantity of that material in the reaction-mixture would be fg, f being a number which, when multiplied into the volume of the aliquot, would give as product the total volume of the diluted reaction mixture.

a. Determination of Hydrogen

Samples were exploded in the presence of excess of air according to the standard method described by Dennis (5). The percent of hydrogen in the gasometer is given by the equation

$$\%(H_2) = \frac{0.667 \times \text{contraction}}{\text{volume of sample}}$$

and the volume V of hydrogen at standard conditions formed by the reaction of the compound under investigation is

$$V = \frac{\text{volume in gasometer} \times \%(H_2) \times 273 \times P}{760 \times (273 + T)}$$

where T is the temperature of the gas in degrees Centigrade, and P is the pressure on the gas in the gasometer after corrections have been applied for the hydrostatic pressure and the aqueous tension of concentrated brine. The number of moles of hydrogen corresponding to the volume V is, of course,

$$\frac{V}{22,400}.$$

b. Determination of Sodium Carbonate

Aliquots were treated with excess sulfuric acid, and the carbon dioxide evolved was absorbed by ascarite in an absorption train as described by Fales (6). The number of moles, M, of sodium carbonate present in the reaction mixture is then obtained from the equation

$$M = \frac{\text{grams of evolved carbon dioxide} \times f}{44}$$

It was necessary to determine, by the same method, the amount of sodium carbonate in the 350 grams of stock sodium hydroxide used, and to subtract this blank from the total carbonate M in order to obtain the number of moles of sodium carbonate formed in the reaction. Hence, if a given weight g of stock hydroxide yielded a grams of carbon dioxide, then the number of moles, m, of sodium carbonate present in 350 grams of the stock is given by the equation

$$m = \frac{350 \times a}{44 \times g}$$

and the number of moles of sodium carbonate resulting from reaction is M−m.

c. Determination of Sodium Formate

Aliquots were first treated, according to a standard method (7), with excess hydrochloric acid and mercuric chloride in the presence of a few grams of sodium acetate, then were heated on a water-bath under a reflux condenser for two to three hours. The calomel precipitated according to the equation

$$HCOOH + 2HgCl_2 \rightarrow 2HgCl\downarrow + CO_2 + 2HCl$$

was collected in Gooch crucibles, dried, and weighed. The number of moles M of sodium formate present in the reaction mixture is then calculated by means of the formula

$$M = \frac{\text{weight of HgCl obtained} \times f}{2 \times 236.1}$$

d. Determination of Sodium Glycollate

Aliquots were subjected to a permanganate-oxalate procedure modelled after that described by Scott (8) for the determination of sodium formate. Scott's procedure involves, first, the oxidation of the formate with alkaline permanganate; second, the addition of excess acid and oxalate; and third, the titration with further permanganate of the excess oxalate. In the present application of this procedure, the aliquot, which is already alkaline by reason of the large excess of sodium hydroxide used in the original charge, is treated with a known excess of standard permanganate solution which is about 0.3 normal in acid titrations. The beaker is then heated on the hot-plate for two to three hours. When excess sulfuric acid is now added, manganese dioxide precipitates, and is dissolved by adding a known excess of an approximately 0.25 normal sodium oxalate solution whose strength in terms of the standard permanganate has been determined. The determination is finished by titrating the excess of oxalate in the now acid solution with the standard permanganate. In the calculation of the results, the volume of permanganate equivalent to the volume of oxalate used is subtracted from the total volume of permanganate required in the determination. If the remaining volume is V cc of permanganate of normality N, then the number of moles, M, of sodium glycollate present in the reaction mixture, is given

by the equation

$$M = \frac{f \times V \times N \times 0.01633}{98} .$$

This same procedure was also found to give good results in the determination of ethylene glycol. If an aliquot of a reaction-mixture containing ethylene glycol was equivalent to V' cc of the permanganate solution of normality N, then the number of moles, M', of ethylene glycol present in the reaction mixture is obtained by the formula

$$M' = \frac{f \times V' \times N \times 0.0062}{62} .$$

e. Determination of Sodium Oxalate and Sodium Glycollate in the Presence of Each Other

The reaction-mixtures obtained from the glyoxylic acid runs contained quantities of both sodium oxalate and sodium glycollate. The method adopted to estimate the respective yields of these salts was to determine the total quantity of oxalate plus glycollate, and then to obtain the yield of glycollate by subtracting the amount of oxalate found in a separate analysis.

To put this plan into practise, aliquots were subjected to the above described alkaline permanganate oxidation procedure (d). The net volume V of N normal permanganate required by the sample was then equivalent to the sum of the amounts of oxalate and glycollate present.

When other aliquots of equal volume were titrated with the standard permanganate in acid solution (after the addition of manganese sulfate), it was found that as long as oxalate was present the glycollate was scarcely attacked by the oxidizing agent, so that a pink end-point was obtained which corresponded to the oxidation of all the oxalate and but very little of the glycollate. If the volume v of permanganate of normality N used in this titration is considered to be equivalent to the amount of oxalate present, then the number of moles of oxalate, M, and of glycollate, M', present in the reaction mixture, are obtained from the following formulae:

$$M = \frac{v \times N \times f \times 0.067}{134}$$

$$M' = \frac{(V-v) \times N \times f \times 0.01633}{98}$$

f. Determination of Sodium Lactate

The procedure followed was that described and recommended by Stamm (9) (English translation by R. E. Oesper).

The aliquot, itself alkaline, was pipetted into a large excess of 0.1 molar alkaline permanganate. Under the condition of a large excess of alkaline permanganate, the lactate is oxidized to acetate, while an equivalent quantity of permanganate is reduced to manganate. After the reaction mixture has stood for twenty minutes at room temperature, excess sulfuric acid and 0.25 molar sodium oxalate are added to the solution, then the determination is finished

by titrating the excess of oxalate with V cc of permanganate of normality N.

Before calculating the amount of lactate present, the "blank consumption" is determined as described by Stamm, by reacting, in the absence of an aliquot, the same volumes of oxalate and permanganate as were used in the actual determination, then titrating the excess oxalate with the standard permanganate. This "blank consumption", a volume of b cc, is less than the volume V cc used in the actual determination of lactate, by the number of cubic centimeters of the standard permanganate required to oxidize the lactate in acid solution. Hence the amount of lactate in the aliquot is equivalent to (V—b) cc of the standard permanganate of normality N, and the number of moles, M, of sodium lactate in the total volume of the reaction mixture follows from the formula

$$M = \frac{f \times (V-b) \times N \times 0.032}{128} .$$

This same procedure was also found to give good results in the determination of glycerine. If an aliquot of a reaction-mixture containing glycerine is equivalent to V' cc of the permanganate solution of normality N, then the number of moles, M', of glycerine present in the reaction mixture is obtained by means of the formula

$$M' = \frac{f \times (V-b) \times N \times 0.00658}{92.06} .$$

IV

EXPERIMENTAL

The experimental section of this thesis resolves itself into five parts, one for each of the five compounds studied, namely, (A) sodium formate, (B) formaldehyde, (C) glyoxylic acid, (D) ethylene glycol, and (E) glycerine. Each section presents:

1. A recapitulation of previous reactions of the compound with either fused alkali or caustic solution or both;
2. The equations for the reactions most likely to occur as derived by the application of the fundamental concepts and reaction-mechanism schemes previously developed, to the structural formula of each compound investigated; and
3. The correlation of these postulated equations with the experimental data in relation to both the occurrence and the extent of the occurrence of the reactions.

A. Sodium Formate

The thermal decomposition of sodium formate yields, depending upon the temperature, varying proportions of sodium oxalate, sodium carbonate, carbon monoxide, carbon dioxide, and hydrogen (10).

Fry (11) showed that sodium formate reacts with

fused sodium hydroxide according to the equation

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \qquad (A).$$

The present study shows that in strong aqueous sodium hydroxide solution, sodium formate reacts quantitatively according to this same equation. It is certain that in the aqueous medium sodium oxalate is not an intermediate product, even though the observed quantitative yield of hydrogen could be accounted for by the following reaction scheme:

$$2HCOONa \rightarrow H_2 + (COONa)_2 \qquad (a)$$

$$(COONa)_2 + 2HONa \rightarrow H_2 + 2Na_2CO_3 \qquad (b)$$

$$\sum(a,b) \quad 2HCOONa + 2HONa \rightarrow 2H_2\uparrow + 2Na_2CO_3 \qquad (A)$$

This observation is made because sodium oxalate was shown not to react with thirty-five normal sodium hydroxide solution. Hence, if oxalate were formed in the reaction of sodium formate with alkali, it would then remain and be found in appreciable quantities in the reaction mixture. But only traces of oxalate could be detected.

Since sodium formate reacts directly with concentrated sodium hydroxide solution in conformity with equation (A), the following experiments were conducted to determine the effect of the presence of piperidine upon the extent of occurrence of this reaction.

The effect of piperidine was investigated because Fry, Cameron, and Bowman (2) previously showed that the presence of the organic bases pyridine, aniline, quinoline,

mono- and di-methyl aniline, and isoamyl-amine, increased the extent of occurrence of the reduction of nitrobenzene to azoxybenzene according to the Klinger reaction discussed in Section I. It was then thought that these organic bases increased the extent of the occurrence of the reaction by promoting the extent of the acidic dissociation of sodium hydroxide. But preliminary experiments with pyridine present in the thirty-five normal aqueous sodium hydroxide solution yielded decreased amounts of hydrogen. This was entirely unexpected. To be sure that the decreased yield of hydrogen was not due to the reduction of pyridine by hydrogen, runs were then conducted using piperidine in place of pyridine, and again it was found that the extent of occurrence of the reaction in aqueous solution was decreased, whereas formerly in methyl alcohol solution it was increased by the presence of organic bases.

To quantitatively measure this effect of piperidine, two runs, I and II, each in duplicate, were conducted using 13.6 grams, or 0.2 mole, of sodium formate in the standard sodium hydroxide solution. To the reaction mixtures in runs II there was added 5 cc of piperidine. The reaction-mixtures were maintained at 250° for 8.5 hours, at the end of which time the evolution of hydrogen had ceased in runs I, but not in runs II. This shows that the presence of piperidine had definitely retarded the rate of the reaction. The extent of the occurrence of the reaction (A) in runs I without, and in runs II with, piperidine is shown by the data in the

following Table I, which data was determined by methods herein previously described:

TABLE I

Experimental data based upon the reaction of 0.2 mole of sodium formate according to equation (A): $HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow$

Run	Na_2CO_3 found (moles)	Na_2CO_3 % theory	H_2 found (moles)	H_2 % theory	HCOONa remaining (moles)	HCOONa % reacted
Ia	0.169	84.7	0.170	85.0	0.018	90.8
Ib	0.171	85.3	0.171	85.3	0.015	92.3
IIa	0.029	14.4	0.028	14.0	0.168	16.1
IIb	0.032	16.2	0.030	15.2	0.164	18.2

The above data shows that, since the percent theory yields of the sodium carbonate and hydrogen are practically identical, that is, the ratios of carbonate to hydrogen are 1:1, it is evident that the reaction occurs in conformity with equation (A). However, while 85% of the sodium formate reacts in the thirty-five normal sodium hydroxide solution according to the postulated equation (A), the extent of the occurrence of this reaction is reduced to 15% by the presence in the reaction mixture of a small amount, only 5 cc, of piperidine.

In order to explain this inhibitive action of pyridine and piperidine, the following assumption is proposed:

The equation for the acidic dissociation of sodium hydroxide may be written—

$$HONa \rightleftharpoons \overset{+}{H} + \overset{-}{O}Na$$

Now the organic base RNH may use up the $\overset{+}{H}$ so that it is no longer available for the liberation of hydrogen from carbon compounds, by adding the $\overset{+}{H}$ and $\overset{-}{O}Na$ to form a salt similar to the familiar hydrochloride, thus:

$$RNH + \overset{+}{H} + \overset{-}{O}Na \rightarrow RNH_2ONa \rightleftharpoons R\overset{+}{N}H_2 + \overset{-}{O}Na$$

The $\overset{+}{H}$ is now replaced by $R\overset{+}{N}H_2$. Since it is likely that there were but traces of $\overset{+}{H}$ originally present, and since the dissociation of the weak acid HONa into $\overset{+}{H}$ and $\overset{-}{O}Na$ would be repressed by the presence of the salt RNH_2ONa, it may be concluded that a drop of piperidine would greatly decrease the concentration of the $\overset{+}{H}$ dissociating from the sodium hydroxide by forming $R\overset{+}{N}H_2$, which would then be unable to react to liberate hydrogen from organic compounds.

Use of the fact that piperidine inhibits or limits the extent of the occurrence of a reaction may be made in the interpretation of reaction-mechanisms involving reactions of organic compounds with alkali. For instance, if a system of postulated equations should include as an intermediate product sodium formate, or indeed any other compound that will not react with alkali in the presence of piperidine, then simple addition of this base should permit the identification of the formate or other compound in the final reaction mixture.

B. Formaldehyde

With fused alkali formaldehyde reacts thus (12):

$$HCHO + 2HONa \rightarrow Na_2CO_3 + 2H_2\uparrow \qquad (A).$$

In aqueous solution, alkali and formaldehyde undergo the familiar Cannizarro reaction. Fry, Price, and Uber (3) showed that this reaction occurs according to the following scheme:

$$HCHO + HONa \rightarrow HCOONa + 2H \qquad (a)$$

$$HCHO + 2H \rightarrow CH_3OH \qquad (b)$$

$$\Sigma(a,b) \quad 2HCHO + HONa \rightarrow HCOONa + CH_3OH \qquad (B)$$

The actual liberation of hydrogen gas, as first noted by Loew (13) in 1887, proves the occurrence of an intermediate reaction, equation (a). Whenever the reaction of formaldehyde and sodium hydroxide is accompanied by the liberation of hydrogen, this reaction in the present and subsequent discussions will be represented by and referred to as equation (C), wherein hydrogen is represented by the molecular formula, H_2:

$$HCHO + HONa \rightarrow HCOONa + H_2\uparrow \qquad (C).$$

It was previously shown (3) that when formaldehyde is boiled with 2.5 normal sodium hydroxide solution containing cupric oxide, sodium formate and methyl alcohol, copper, and free hydrogen are the products of the interactions. The formation of these four products was explained by the

division of the total amount of hydrogen rendered available by the occurrence of (a) into three fractions, one of which effected the reduction of the remaining formaldehyde to methyl alcohol (Equation b), while another brought about the reduction of cupric oxide to copper, and the final fraction was liberated as gas (Equation C). By quantitatively estimating the amounts of sodium formate, methyl alcohol, copper, and free hydrogen obtained from a known initial amount of formaldehyde, the percent extent of occurrence of each of the four reactions leading respectively to the formation of the four products indicated, was obtained.

Considering now the action of thirty-five normal sodium hydroxide solution upon formaldehyde, the following three possibilities call for discussion:

1. If two moles of formaldehyde should react with the standard thirty-five normal sodium hydroxide solution to the extent of 100% according to the summation-equation (B), then one mole each of sodium formate and methyl alcohol would be formed. How then would each of these two products react with the alkali. Sodium formate readily reacted to give hydrogen and sodium carbonate in conformity with equation (D),

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \qquad (D),$$

as has already been described in part (A); but on the other hand, methyl alcohol, when heated in a caustic solution of the standard concentration, was found not to react. Hence, it follows that two moles of formaldehyde, reacting 100% according

to equation (B), would yield one mole of sodium formate, which in turn reacting according to equation (D) would yield one mole of hydrogen gas.

2. If on the other hand one mole of formaldehyde should react in the thirty-five normal alkali to the extent of 100% according to equation (C), then one mole each of hydrogen and sodium formate would be formed; and, in turn, the mole of formate could then react in conformity with equation (D) to yield one mole each of hydrogen and sodium carbonate. Hence, it follows that one mole of formaldehyde reacting 100% according to equation (C) would eventually liberate <u>two</u> moles of hydrogen in accordance with equation (A), which is the summation of equations (C) and (D), thus:

$$HCHO + HONa \rightarrow HCOONa + H_2 \qquad (C)$$

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2 \qquad (D)$$

$$\Sigma(C, D) \qquad HCHO + 2HONa \rightarrow Na_2CO_3 + 2H_2\uparrow \qquad (A).$$

3. If, as the third possibility, a fraction of a mole of formaldehyde should react according to equation (C), and the remainder of the mole according to (B), then a net evolution of more than 0.5 but less than two moles of hydrogen would be obtained, because the methyl alcohol formed in conformity with equation (B) would not react to yield hydrogen.

Now since in the actual experiments performed, 0.2 mole of formaldehyde yielded more than 0.1 but less than 0.4 of a mole of hydrogen, the occurrence of all three of the reactions (B), (C), and (D), was indicated.

In summary, the equations for three inter-related reactions must be taken into account, namely,

$$2HCHO + HONa \rightarrow HCOONa + CH_3OH \qquad (B)$$

$$HCHO + HONa \rightarrow HCOONa + H_2\uparrow \qquad (C)$$

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \qquad (D)$$

Equation (B), which is the Cannizarro reaction, is held to be concurrent with equation (C), which represents the direct liberation of free hydrogen from formaldehyde. Equation (D) is then consecutive to both equations (B) and (C). It represents the conversion to carbonate of the formate formed through the occurrence of the reactions represented by the equations (B) and (C).

Wherefore, to determine the extent of the occurrence of each of the three reactions (B), (C), and (D) under various experimental conditions, three runs, I, II, and III, were conducted in duplicate. The source of formaldehyde in runs I and II was trioxymethylene; in run III, formalin solution. The reaction-mixtures in runs II and III contained piperidine.

In runs I, 0.2 mole of trioxymethylene was heated with the thirty-five normal alkali solution for 16 hours at 250°C.

In runs II, in addition to the alkali and the 0.2 mole of trioxymethylene, there was added five cc of piperidine. This reaction-mixture was also heated for 16 hours at 250°C.

In runs III, 15 cc of formalin solution, analyzed in accordance with the acidimetric method of Williams (14), was

dropped from a constant-pressure Walther funnel into the standard concentrated sodium hydroxide solution, containing 5 cc of piperidine, over a period of 20 hours while maintaining the temperature at 215°C.

In order to calculate the extent of the occurrence of the reactions (B), (C), and (D), the experimental data obtained by the methods of analysis for hydrogen and carbonate given in Section IIIB, was correlated according to the following mathematical development:

If c moles of sodium carbonate and h moles of hydrogen are formed from k moles of formaldehyde, then the number of moles of hydrogen formed in accordance with equation (C) is given by the quantity (h—c), so that the percent of the total formaldehyde, %(C), reacting in accordance with equation (C), is given by the equation,

$$\%(C) = \frac{100\ (h-c)}{k}\ .$$

The percent of the total formaldehyde used up by the Cannizarro reaction (B), %(B), can then be obtained from the following equation:

$$\%(B) = 100-\%(C).$$

The percent occurrence of reaction (D) to form sodium carbonate must be based on the total number of moles of formate, t, available through the occurrence of (B) and (C). The quantity t is the sum of (h—c), the moles of formate resulting from the occurrence of (C), plus half the number of moles of formaldehyde which react according to equation (B), that is,

$\frac{k-(h-c)}{2}$. Hence

$$t = h-c + \frac{k-(h-c)}{2}$$

$$= \frac{k + (h-c)}{2}$$

It follows that the percent of the total formate reacting in conformity with equation (D) is given by the equation,

$$\%(D) = \frac{100c}{t} .$$

The data as correlated in accordance with this development is presented in the following Table II:

TABLE II

Experimental data based upon the reaction of formaldehyde according to equations (B), (C), and (D):

$$2HCHO + HONa \rightarrow HCOONa + CH_3OH \quad (B)$$
$$HCHO + HONa \rightarrow HCOONa + H_2\uparrow \quad (C)$$
$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \quad (D)$$

1	2	3	4	5	6
Run	Temp. and Time	CH_2O used (moles) (k)	H_2 found (moles) Eq.'s C and D (h)	Na_2CO_3 found (moles) Eq. D (c)	CH_2O (moles) Eq. C (h—c)
Ia	250° 16 hrs.	0.2000	0.0798	0.0763	0.0034
Ib	250° 16 hrs.	0.2000	0.0819	0.0794	0.0025
IIa	250° 16 hrs.	0.2000	0.0392	0.0251	0.0141
IIb	250° 16 hrs.	0.2000	0.0372	0.0279	0.0092
IIIa	215° 20 hrs.	0.1954	0.1368	0.0220	0.1148
IIIb	215° 20 hrs.	0.1954	0.1424	0.0206	0.1218

7	8	9	10	11	12
Run	CH_2O (moles) Eq. B k—(h—c)	HCOONa (moles) Eq. D (t)	% extent Eq. B	% extent Eq. C	% extent Eq. D
Ia	0.1966	0.1017	98.3	1.70	75.1
Ib	0.1975	0.1012	98.8	1.25	78.5
IIa	0.1859	0.1070	93.0	7.05	21.1
IIb	0.1908	0.1046	95.4	4.60	19.5
IIIa	0.0806	0.1551	41.3	58.7	14.2
IIIb	0.0736	0.1586	37.7	62.3	13.0

The above data show:

1. That the extent of the occurrence of the reaction (C) can vary with conditions from 1-62%. The evolution of hydrogen according to this equation may be almost zero, as in runs I. It is favored to some degree by the presence of piperidine, as shown by runs II; and is tremendously increased, as in runs III, if the formaldehyde is brought into contact with the hot sodium hydroxide solution so slowly that at no time is there any large excess of formaldehyde available for reduction to methyl alcohol.

2. That the extent of the occurrence of the theoretical Cannizarro reaction (B) may vary from 99-38%, decreasing in exact conformity with a corresponding increase from 1-62% in the extent of occurrence of reaction (C).

3. That the occurrence of reaction (D), in the absence of piperidine to the extent of 75%, and in the presence of piperidine to the extent of only 10-20%, confirms the result described under division A of this Section, namely, that piperidine inhibits the interaction of sodium formate and sodium hydroxide. Again, as shown by runs III, when piperidine is present and at the same time the temperature is kept comparatively low (215°C.), then the percent conversion of formate to carbonate is only 12-14% of the theory even after twenty hours of heating.

The various reactions of formaldehyde with alkali noted in both previous and present studies, may be summarized as follows:

1. In a 0.5 molar solution of sodium hydroxide, the Cannizarro reaction (B) is complete in accordance with a one to one ratio of methylate to formate, and no hydrogen is evolved. (3)

2. In a 2.5 molar solution of caustic alkali in the presence of cupric oxide, hydrogen gas up to 50% of the amount theoretically possible is obtained by the occurrence of reaction (C); none of this hydrogen results from the conversion of formate to carbonate (Equation D).(3)

3. In a 35 molar solution of sodium hydroxide, under the best conditions, the conversion of formaldehyde according to the Cannizarro reaction (B) is almost theoretical, hydrogen at higher temperatures evolving from the formate which is one of the products. Methyl alcohol, once formed, does not react with the caustic alkali.

4. In concentrated aqueous alkali, the evolution of hydrogen directly from formaldehyde according to equation (C) is favored by slow addition of the formalin to the hot solution, because under these conditions a large excess of aldehyde is never available for reduction to methyl alcohol.

5. In fused alkali formaldehyde is converted quantita-

tively, in conformity with equation (A), to carbonate and hydrogen only.

C. Glyoxylic Acid (Dichloracetic Acid)

When treated with aqueous alkali, glyoxylic acid undergoes the Cannizarro reaction to form oxalic and glycollic acids (15). The following reaction-mechanism scheme may be drawn up to represent the action of alkali on glyoxylic acid. It is entirely parallel to the scheme previously developed for the mechanism of the Cannizarro reaction of formaldehyde:

$$CHOCOONa + HONa \rightarrow (COONa)_2 + 2H \qquad (a)$$

$$\underline{CHOCOONa + 2H \rightarrow CH_2OHCOONa} \qquad (b)$$

$$\sum(a,b)\ 2CHOCOONa + HONa \rightarrow (COONa)_2 + CH_2OHCOONa \qquad (A).$$

Equation (A), the summation of a and b, is the Cannizarro reaction as applied to glyoxylic acid, while equation (B)

$$CHOCOONa + HONa \rightarrow (COONa)_2 + H_2\uparrow \qquad (B)$$

is the same as (a) save that in (B) the liberated hydrogen gas, for purposes of this discussion, is represented, not in statu nascendi, but as free hydrogen, H_2.

Since glyoxylic acid was not available as a reagent, and since dichloracetic acid reacts quantitatively with thirty-five normal sodium hydroxide solution in conformity with the following equation,

$$CHCl_2COOH + 3HONa \rightarrow CHOCOONa + 2H_2O + 2NaCl \qquad (C),$$

dichloracetic acid was used in this investigation as a substitute reagent equivalent mole for mole to glyoxylic acid. In the further discussion, dichloracetic acid will be both regarded and referred to as glyoxylic acid.

When dichloracetic acid was treated with the standard thirty-five normal alkali, the reactions occurring led to the formation of sodium oxalate and sodium glycollate according to equation (A), and of sodium oxalate and hydrogen according to equation (B). It was found in separately conducted experiments that neither sodium oxalate nor sodium glycollate reacted with the sodium hydroxide solution. In separate experiments it was also found that piperidine reacts with dichloracetic acid to form a tarry material, so that the effect of piperidine on the reactions (A) and (B) could not be studied.

In order to determine the extent of the occurrence of reactions (A) and (B), two runs were made, I in duplicate, II a single run.

Runs I were carried out by simply mixing, in the cold, 350 grams of sodium hydroxide, 88cc of water, and 0.1786 moles, or 15 cc, of dichloracetic acid. Without the application of heat hydrogen was spontaneously evolved, and completion of the interaction was shown by the cessation of its liberation. No record was found that described the liberation of hydrogen by the action of sodium hydroxide solution on dichloracetic or glyoxylic acids.

In runsII, 0.1786 moles, or 15 cc, of dichloracetic acid, was added drop by drop, during eight hours, to the standard caustic solution, at a temperature of 236-240°C.

The resulting data, determined by analytical methods previously described, was correlated with equations (A) and (B) in the following manner:

$$2CHOCOONa + HONa \rightarrow (COONa)_2 + CH_2OHCOONa \qquad (A)$$

$$CHOCOONa + HONa \rightarrow (COONa)_2 + H_2\uparrow \qquad (B)$$

If $\underline{h}$ moles of hydrogen and $\underline{o}$ moles of oxalate are formed from $\underline{k}$ moles of glyoxylic acid, then the percent of the total glyoxylic acid, %(B), reacting according to equation (B), is given by the formula

$$\%(B) = \frac{100h}{k}.$$

The percent of the total glyoxylic acid, %(A), reacting in conformity with equation (A), is represented by the formula

$$\%(A) = \frac{200(o-h)}{k}$$

where the quantity (o—h) is the number of moles of oxalate formed in conformity with equation (A). The data so interpreted is shown in the following Table III:

TABLE III

Experimental data based upon the reaction of 0.1786 moles of glyoxylic acid (resulting from dichloracetic acid) in conformity with equations (A) and (B):

$$2CHOCOONa + HONa \rightarrow (COONa)_2 + CH_2OHCOONa \quad (A)$$

$$CHOCOONa + HONa \rightarrow (COONa)_2 + H_2\uparrow \quad (B)$$

1	2	3	4	5	6
Run	Temp. and Time	H_2 found (moles) Eq. B $\underline{h}$	Total $(COONa)_2$ found (moles) $\underline{o}$	$(COONa)_2$ for Eq. A (moles) $\underline{o}-\underline{h}$	CH_2OH-COONa found (moles) Eq. A $\underline{g}$
Ia	cold	0.0347	0.1049	0.0702	0.0755
Ib	cold	0.0281	0.1022	0.0742	0.0779
II	240° 8 hrs.	0.0952	0.1251	0.0299	———

7	8	9	10	11
Run	Ratio $(o-h):g$ theory 1 : 1	% extent A	% extent B	% extent A + % extent B
Ia	1 : 1.07	78.6	19.4	98.0
Ib	1 : 1.05	83.1	15.7	98.8
II	———	33.5	53.3	86.8

The following comments are pertinent to the data in the above Table III:

1. The occurrence of reaction (A) is demonstrated by the approximately one to one ratios (Column 7) of the previously defined quantities (o—h) and g. The occurrence of reaction (B) follows from the evolution of hydrogen accompanied by the formation of an equivalent quantity of sodium oxalate.

2. In runs I, the extent of the occurrence of reaction (A) is about 80% theory; of (B), about 20% theory. The summation of these percentages, by its near approach to 100% (Column 10), supports the reaction-mechanism scheme postulated, since, within the limits of experimental error, all of the glyoxylic acid used is accounted for in terms of the proposed equations (A) and (B).

3. In run II, as contrasted with runs I, the yield of hydrogen in accordance with reaction (B) is very markedly increased from 16 to 53 percent by adding the aldehyde CHOCOOH to the hot caustic solution so slowly that a large excess of it is never available for reduction to sodium glycollate in conformity with the intermediate reaction, equation (b).

4. The reaction of glyoxylic acid with thirty-five normal alkali parallels the reaction-scheme already developed for formaldehyde. The extent of occurrence of the reactions (A) and (B) varies with experimental conditions within the

rather wide limits of 83-33 and 16-53 percent respectively, just as the parallel reactions (A') and (B') with formaldehyde

$$2CH_2O + HONa \rightarrow HCOONa + CH_3OH \qquad (A')$$

$$CH_2O + HONa \rightarrow HCOONa + H_2\uparrow \qquad (B')$$

varied in the extent of their occurrence, as has been described in division B, from 100-38 and 1-62 percent respectively.

D. Ethylene Glycol

The reaction of ethylene glycol with fused caustic alkali has already been discussed in detail in Section II, wherein was presented a reaction-mechanism scheme, which is repeated below. This scheme postulates that a molecule of glycol is equivalent in its reaction with the fused caustic alkali to one molecule each of formaldehyde and methyl alcohol, thus:

$$CH_2OHCH_2OH \quad = = \quad CH_2O + CH_3OH \qquad (a)$$

$$CH_2O + 2HONa \rightarrow Na_2CO_3 + 2H_2\uparrow \qquad (b)$$

$$CH_3OH + 2HONa \rightarrow Na_2CO_3 + 3H_2\uparrow \qquad (c)$$

$$\Sigma(a,b,c) \quad CH_2OHCH_2OH + 4HONa \rightarrow 2Na_2CO_3 + 5H_2\uparrow \qquad (A)$$

However, when glycol reacts with thirty-five normal sodium hydroxide solution, it is found that under these conditions the glycol does not react as noted in equation (a); that is, the carbon-carbon bond is not broken, for, while the oxidation of the glycol does occur, it extends only to

the sodium glycollate stage, with the evolution of two moles of hydrogen per mole of ethylene glycol, according to the following reaction-mechanism scheme:

$$CH_2OHCH_2OH + 2HONa \rightarrow CH_2OHC(OH)(ONa)_2 + 2H_2 \quad (d)$$

$$CH_2OHC(OH)(ONa)_2 \rightarrow CH_2OHCOONa + HONa \quad (e)$$

$$\Sigma(d,e)\quad CH_2OHCH_2OH + HONa \rightarrow CH_2OHCOONa + 2H_2\uparrow \quad (B)$$

In order to determine the extent of the occurrence of reaction (B) both in the presence and in the absence of piperidine, two runs, I and II, each in duplicate, were conducted, using 0.1052 moles of ethylene glycol in the thirty-five normal sodium hydroxide solution. To the reaction mixtures in runs II there was added 5 cc of piperidine. The reaction mixtures were maintained at 250°C. for ten hours, at the end of which time the evolution of hydrogen had ceased in runs I, while in runs II there was noted no evolution of hydrogen whatsoever.

The extent of occurrence of reaction (B) in runs I in the absence, and in runs II in the presence, of piperidine, is shown by the data in the following Table IV, which was determined by methods previously described in Section III:

TABLE IV

Experimental data based upon the reaction of 0.1052 moles of ethylene glycol according to equation (B): $CH_2OHCH_2OH + HONa \rightarrow CH_2OHCOONa + 2H_2\uparrow$.

1	2	3	4	5	6	7
Run	$(CH_2OH)_2$ remaining (moles)	CH_2OH-COONa found (moles)	CH_2OH-COONa % theory	H_2 found (moles)	H_2 % theory	Ratio CH_2OH-COONa: H_2 (theory 1:2)
Ia	_____	0.1048	99.6	0.1996	94.9	1 : 1.91
Ib	_____	0.1043	99.1	0.2026	96.3	1 : 1.94
IIa	0.1064	0.00	00.0	0.00	00.0	————
IIb	0.1065	0.00	00.0	0.00	00.0	————

In the above data, the percent theory yields of the sodium glycollate and hydrogen agree within the limits of experimental error, that is, the ratios of glycollate to hydrogen are one to two. Therefore it is evident that the reaction occurs in conformity with equation (B). However, while in runs I better than 95% of the glycol reacts with the sodium hydroxide according to equation (B), in runs II the extent of the occurrence of reaction (B) is reduced to zero by the presence in the reaction mixture of only 5 cc of piperidine. At the end of the ten hour period of heating, no hydrogen had been evolved and no sodium glycollate was found in the reaction mixture. The glycol remained unchanged in the reaction-mixture and was quantitatively accounted for

by the permanganate-oxalate procedure described in Section III.

E. Glycerine

From the reactions of glycerine with widely varying quantities of sodium hydroxide, various investigators, employing various reaction-temperatures ranging from 200-500°, have obtained the following reaction-products: hydrogen, methane, liquid olefines, propylene glycol, ethyl, propyl, isopropyl, methyl, and allyl alcohols, and the salts—sodium carbonate, acetate, propionate, butyrate, formate, oxalate, lactate, and acrylate (16-23).

Fry and Schulze[24] reacted glycerine with a large excess of fused sodium hydroxide at 450°C. under conditions insuring the complete interaction and collection of all the products, and thereby obtained data indicating that of the total amount of glycerine used, 21% reacted according to the following equation (A) and 78% in conformity with the following equation (B):

$$C_3H_5(OH)_3 + 6HONa \rightarrow 3\ Na_2CO_3 + 7H_2\uparrow \qquad (A)$$

$$C_3H_5(OH)_3 + 4HONa \rightarrow 2Na_2CO_3 + 3H_2\uparrow + CH_4\uparrow + H_2O \qquad (B)$$

A review of the method of deriving equations (A) and (B) by application of the rule and principles described in Section II, and illustrated by the reactions of ethylene glycol, is now pertinent to the discussion of the reactions of glycerine with concentrated aqueous alkali solution.

"In equation (A), 21% of the glycerine used was completely oxidized to carbonate with the liberation of seven

molecules of hydrogen from one molecule of glycerine. The rule directly applied calls for five molecules, but here the glycerine molecule is apparently equivalent in its reaction to one molecule of methyl alcohol plus two molecules of formaldehyde, the former according to rule yielding three, while the latter yields four, that is, a sum total of seven molecules of hydrogen as actually determined. This fact is summarized in the following reaction-scheme:

$$C_3H_5(OH)_3 \rightleftharpoons CH_3OH + 2CH_2O \qquad (a)$$

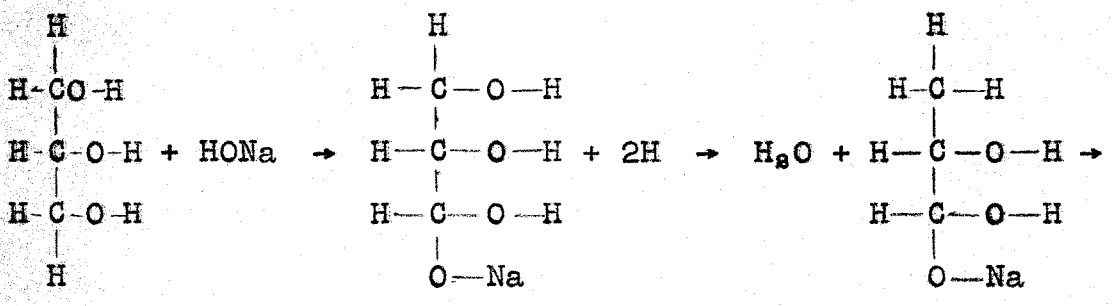
$$CH_3OH + 2MOH \rightarrow M_2CO_3 + 3H_2\uparrow \qquad (b)$$

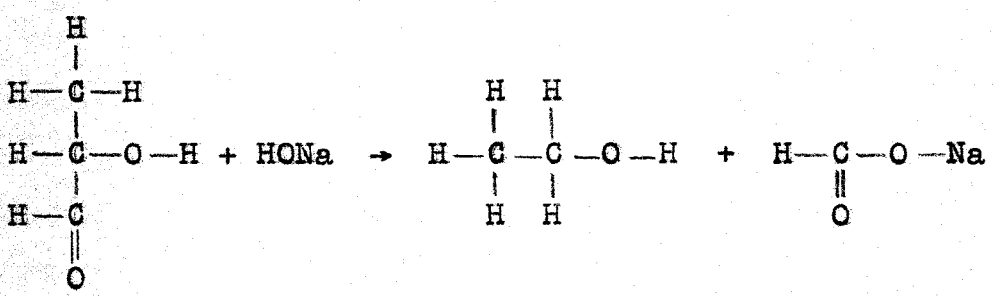
$$2CH_2O + 4MOH \rightarrow 2M_2CO_3 + 4H_2\uparrow \qquad (c)$$

$$\Sigma(a,b,c) \quad C_3H_5(OH)_3 + 6MOH \rightarrow 3M_2CO_3 + 7H_2\uparrow \qquad (A)$$

"Furthermore, according to equation (B), 78% of the glycerine used was not completely oxidized to carbonate, since some of its carbon was liberated as methane, that is, one molecule of glycerine yielded one molecule of methane and three molecules of hydrogen. To account for the liberation of methane, the rule requires that the glycerine molecule must react as if it were equivalent to other molecules, one of which embodies a methyl radical. Such would be the case provided that the glycerine underwent an oxidation-reduction change. This is readily conceivable in terms of the type reaction, RH + HOM → ROM + 2H, which may involve a hydrogen atom at an end carbon of the molecule. The hydrogen so formed is not necessarily liberated, but effects the reduction of a (CH_2OH) radical at the other end of the mole-

cule, forming a (CH_3) radical, thus: $RCH_2OH+2H \rightarrow RCH_3+H_2O$. This oxidation-reduction change may be represented thus:





"Accordingly, the glycerine molecule could react as equivalent to one molecule of ethyl alcohol plus one molecule of formic acid. As previously shown, and in conformity with the rule, a molecule of ethyl alcohol yields one of methane and two of hydrogen, while the formic acid molecule yields one of hydrogen, that is, a total, as indicated in the verified glycerine equation (B), of one molecule of methane and three of hydrogen. This fact is summarized in the following reaction-scheme: (4)

$$C_3H_5(OH)_3 \rightarrow CH_3CH_2OH + HCOOH \qquad (a)$$

$$CH_3CH_2OH + 2MOH \rightarrow M_2CO_3 + CH_4 + 2H_2 \qquad (b)$$

$$HCOOH + 2MOH \rightarrow M_2CO_3 + H_2O + H_2 \qquad (c)$$

$$\Sigma(a,b,c)\ C_3H_5(OH)_3 + 4MOH \rightarrow 2M_2CO_3 + CH_4 + 3H_2 + H_2O \qquad (B)".$$

By the further application of the principles illustrated in the above quotation, the following reaction-schemes, accounting for the formation of certain intermediate oxidation products of glycerine, may be derived:

If glycerine should be oxidized by caustic alkali to glyceric acid, four atoms of hydrogen would be available, thus:

$$CH_2OHCHOHCH_2OH + 2HONa \rightarrow CH_2OHCHOHC(OH)(ONa)_2 + 4H \quad (g)$$

$$CH_2OHCHOHC(OH)(ONa)_2 \rightarrow CH_2OHCHOHCOONa + HONa \quad (h)$$

$$\Sigma(g,h)\ CH_2OHCHOHCH_2OH + HONa \rightarrow CH_2OHCHOHCOONa + 4H \quad (C)$$

These four atoms of hydrogen might be liberated as two molecules of hydrogen gas, as shown in equation (D), wherein hydrogen is represented by the molecular formula, H_2, thus:

$$CH_2OHCHOHCH_2OH + HONa \rightarrow CH_2OHCHOHCOONa + 2H_2\uparrow \quad (D).$$

On the other hand, two of the four hydrogen atoms might reduce glyceric acid to lactic acid (equation E), or to hydracrylic acid (equation F), and only the other two atoms be liberated as <u>one</u> molecule of hydrogen gas, thus:

$$CH_2OHCHOHCOONa + 4H \rightarrow CH_3CHOHCOONa + H_2O + H_2\uparrow \quad (E)$$

$$CH_2OHCHOHCOONa + 4H \rightarrow CH_2OHCH_2COONa + H_2O + H_2\uparrow \quad (F)$$

It is further possible that all four hydrogen atoms might be active in reducing glyceric acid to <u>propionic</u> acid, with the result that no hydrogen gas would be liberated, as indicated in equation (G):

$$CH_2OHCHOHCOONa + 4H \rightarrow CH_3CH_2COONa + 2H_2O \quad (G)$$

The further reaction of the sodium hydracrylate formed in equation (F) to yield sodium carbonate and sodium acetate could occur according to the following scheme:

$$CH_2OHCH_2COONa + 2HONa \rightarrow C(ONa)_2(OH)CH_2COONa + 2H_2 \quad (i)$$

$$C(ONa)_2(OH)CH_2COONa \rightarrow\rightarrow COONaCH_2COONa + HONa \quad (j)$$

$$COONaCH_2COONa + HONa \rightarrow Na_2CO_3 + CH_3COONa \quad (k)$$

$$\sum(i,j,k)\ CH_2OHCH_2COONa + 2HONa \rightarrow Na_2CO_3 + CH_3COONa + 2H_2\uparrow \quad (H)$$

On the other hand, the further reaction of the sodium lactate formed according to equation (E) to yield also the same products, sodium carbonate and sodium acetate, according to the identical summation-equation (H), could occur as follows:

$$CH_3CHOHCOONa + HONa \rightarrow Na_2CO_3 + CH_3CH_2OH \quad (m)$$

$$CH_3CH_2OH + 2HONa \rightarrow CH_3C(OH)(ONa)_2 + 2H_2 \quad (n)$$

$$CH_3C(OH)(ONa)_2 \rightarrow CH_3COONa + HONa \quad (o)$$

$$\sum(m,n,o)\ CH_3CHOHCOONa + 2HONa \rightarrow Na_2CO_3 + CH_3COONa + 2H_2\uparrow \quad (H).$$

In preliminary runs it was found that glycerine reacts with thirty-five normal sodium hydroxide solution at 250° with the evolution of hydrogen and the formation of sodium carbonate, sodium acetate, sodium propionate, and sodium lactate. It has just been shown how the application of the general type reaction to the glycerine molecule may serve to explain in terms of reaction-mechanism schemes the formation of each of these reaction-products.

The above summation-equations, (C), (E), and (H),

according to which these several products are formed, may now be resolved into two other equations, (J) and (K), which will serve to correlate the quantitative yields of the several reaction-products with the extent of occurrence of the postulated reactions.

Accordingly, the formation of sodium lactate with evolution of hydrogen may be represented by equation (J), the summation of equations (C) and (E), thus:

$$CH_2OHCHOHCH_2OH + HONa \rightarrow CH_2OHCHOHCOONa + 4H \quad (C)$$

$$CH_2OHCHOHCOONa + 4H \rightarrow CH_3CHOHCOONa + H_2O + H_2 \quad (E)$$

$$\Sigma(C,E) \quad CH_2OHCHOHCH_2OH + HONa \rightarrow CH_3CHOHCOONa + H_2O + H_2\uparrow \quad (J)$$

Furthermore, the concurrent formation of sodium acetate and sodium carbonate, also accompanied by the liberation of hydrogen, may be represented by equation (K), the summation of equations (J) and (H), thus:

$$CH_2OHCHOHCH_2OH + HONa \rightarrow CH_3CHOHCOONa + H_2O + H_2 \quad (J)$$

$$CH_3CHOHCOONa + 2HONa \rightarrow Na_2CO_3 + CH_3COONa + 2H_2 \quad (H)$$

$$\Sigma(J,H) \quad CH_2OHCHOHCH_2OH + 3HONa \rightarrow Na_2CO_3 + CH_3COONa + 3H_2\uparrow \quad (K)$$

In order to prove the occurrence and determine the extent of the occurrence of the reactions represented by the equations (J) and (K), both in the absence and in the presence of piperidine, three runs, I, II, and III, each in duplicate, were conducted with the thirty-five normal sodium hydroxide solution. Piperidine (5 cc) was used only in runs III. The reaction mixtures in all three pairs of runs were heated for

ten hours at 250° C., at the end of which time the evolution of hydrogen in runs I and II had ceased. In runs III, piperidine present, the rate of evolution of hydrogen was markedly slow throughout the entire period of heating, and the total volume of hydrogen was only about 1/20 the volume of hydrogen evolved in runs I and II during the ten hour period of heating allotted to these experiments.

The resulting data, determined by the analytical procedures previously described, is summarized in the following Table V:

TABLE V

Experimental data based upon the reaction of glycerine according to the following equations:

$C_3H_5(OH)_3 + HONa \rightarrow CH_3CHOHCOONa + H_2O + H_2\uparrow$ (J)

$C_3H_5(OH)_3 + 3HONa \rightarrow CH_3COONa + Na_2CO_3 + H_2O + 3H_2\uparrow$ (K)

1	2	3	4	5	6	7
Run	$C_3H_5(OH)_3$ used (moles)	$C_3H_5(OH)_3$ remaining (moles)	CH_3CHOH-COONa found (moles) Eq.(J)	Na_2CO_3 found (moles) Eq.(K)	% extent (J)	% extent (K)
Ia	0.0622	———	0.0283	0.0289	45.5	46.4
Ib	0.0642	———	0.0299	0.0275	46.6	42.8
IIa	0.1202	———	0.0948	0.0348	78.9	29.0
IIb	0.1203	———	0.0959	0.0350	79.7	29.1
IIIa	0.1321	0.1212	———	———	———	———
IIIb	0.1321	0.1231	———	———	———	———

8	9	10	11	12	13	14
Run	% extent (J) + % extent (K)	Yield H_2 (calc.) $\rightleftharpoons$ CH_3CHOH-COONa Eq. (J) (moles)	Yield H_2 (calc.) $\rightleftharpoons$ Na_2CO_3 Eq. (K) (moles)	Total H_2 (calc.) Eq. (J) + (K) (moles)	Total H_2 found (moles)	Ratio H_2 found to H_2 calc. theory 1 : 1
Ia	91.9	0.0283	0.0867	0.1156	0.1155	1:1.00
Ib	89.4	0.0275	0.0825	0.1124	0.1220	1:0.93
IIa	107.9	0.0948	0.1044	01992	0.1972	1:1.01
IIb	108.8	0.0959	0.1050	0.2009	0.1990	1:1.01
IIIa	———	———	———	———	0.0151	———
IIIb	———	———	———	———	0.0108	———

The above data indicate the following conclusions:

1. The sums of the percent extents of the occurrence of the reactions represented by the equations (J) and (K) in runs I and II (Column 8) are in approximate agreement.

2. The total calculated yields of hydrogen (Column 11) available through the occurrence of reactions (J) and (K) are practically identical with the total yields of hydrogen found (Column 12). The yields of hydrogen found and calculated stand to one another as one to one (Column 13).

3. In runs Ia and b, the percent extents of occurrence of reactions (J) and (K) are almost identical, and each is less than 50% complete. In runs IIa and b, the percent extent of occurrence of reaction (K) is almost three times as great as that of reaction (J). This difference may be related to the fact that in runs I the amount of glycerine used was only half the amount used in runs II.

4. It is very evident that the presence of piperidine, used in runs IIIa and b, inhibits these reactions of glycerine and sodium hydroxide, for in these runs more than 90% of the glycerine was found to be unreacted at the end of the allotted ten hour period of heating at 250°. This inhibition is further attested by a comparison of the yields of hydrogen evolved in runs I and II in the absence of piperidine with the yield of hydrogen in runs III in the presence of piperidine. Thus in the three runs the average yields of hydrogen <u>per mole</u> of glycerine stand in the following ratios:

Runs I	1.9 : 1
Runs II	1.7 : 1
Runs III	0.1 : 1

It is thus evident that the amount of hydrogen evolved in the presence of piperidine is only 5-6% of the amount obtainable under the same conditions in the absence of piperidine.

Note 1: The sum of the extents of occurrence of (J) and (K) in runs I (Column 8) accounts for 90% of the glycerine used. Since sodium propionate, in small quantity, insufficient to be determined, was definitely shown to be one product of the reaction, it may be that the remaining 10% of glycerine in runs I was converted to this salt in conformity with equation (G).

Note 2: On the other hand, the sum of the percent extents of occurrence of reactions (J) and (K) in runs II (Column 8), averaging 108%, is considerably over 100%. This may be explained by the assumption that some of the glycerine in these runs remained unreacted, and hence participated in the permanganate titration which was conducted to determine the yield of lactate. Glycerine requires for its complete oxidation 3.5 times the volume of permanganate needed to oxidize a corresponding molar quantity of sodium lactate.

V

SUMMARY AND CONCLUSIONS

The action of a thirty-five normal solution of sodium hydroxide upon (A) sodium formate, (B) formaldehyde, (C) glyoxylic acid, (D) ethylene glycol, and (E) glycerine, was quantitatively investigated. The application to the structural formula of each of these five compounds of the type reaction $RH_n + nMOH \rightarrow R(OM)_n + mH_2\uparrow$, in which the principle of the apparent acidic dissociation of sodium hydroxide is implicit, led to the development, for each compound investigated, of a reaction-mechansim scheme, whence followed a summation-equation or equations for reactions whose occurrence and the extent thereof were correlated with the experimental data. It was found that the presence of piperidine in a reaction-mixture inhibited the extent of the occurrence of certain reactions.

The following conclusions are in accord with the observations made and the experimental data obtained:

A. Sodium Formate

1. Reaction occurred to the extent of 85% of the theory according to the equation

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \qquad (A).$$

2. In the presence of piperidine, this reaction (A) occurred only to the extent of 16%.

B. Formaldehyde

1. Reaction proceeded in conformity with three equations:

$$2HCHO + HONa \rightarrow HCOONa + CH_3OH \qquad (B)$$

$$HCHO + HONa \rightarrow HCOONa + H_2\uparrow \qquad (C)$$

$$HCOONa + HONa \rightarrow Na_2CO_3 + H_2\uparrow \qquad (D).$$

The concurrent reactions (B) and (C), under various experimental conditions, occurred to the extent of from 99 to 38% and 1 to 62% of the theory, respectively. The consecutive reaction (D) occurred to the extent of 77% of theory.

2. The presence of piperidine had little or no effect on the extent of occurrence of reactions (B) and (C), but limited the occurrence of (D) to 12-20% of the sodium formate available for reaction.

C. Glyoxylic Acid

1. Reaction occurred in conformity with two equations:

$$2CHOCOONa + HONa \rightarrow (COONa)_2 + CH_2OHCOONa \qquad (E)$$

$$CHOCOONa + HONa \rightarrow (COONa)_2 + H_2\uparrow \qquad (F)$$

The extent of occurrence of these concurrent reactions ranged from 83-33 and 16-53% of the theory respectively, under various experimental conditions.

2. The behavior of this compound in the thirty-five normal caustic solution was entirely analogous to that of formaldehyde.

3. The inhibiting effect of piperidine could not here be studied because of its extensive reaction directly with the reagent, dichloracetic acid.

D. Ethylene Glycol

1. Reaction occurred to the extent of 95% of the theory according to the equation

$$(CH_2OH)_2 + HONa \rightarrow CH_2OHCOONa + 2H_2\uparrow \qquad (G).$$

2. The presence of piperidine apparently completely inhibited this reaction.

E. Glycerine

1. Reactions proceeded in conformity with two equations:

$$C_3H_5(OH)_3 + HONa \rightarrow CH_3CHOHCOONa + H_2\uparrow \qquad (H)$$

$$C_3H_5(OH)_3 + 3HONa \rightarrow CH_3COONa + Na_2CO_3 + 3H_2\uparrow \qquad (J)$$

2. In one run, the average extent of occurrence of the reactions represented by the equations (H) and (J) was 46% and 44% respectively. In another run, wherein a greater quantity of glycerine was used, the extents were 79% and 29% respectively.

3. The presence of piperidine limited the occurrence of both reactions (H) and (J) to the extent that, at the end of the allotted period of heating, more than 90% of the glycerine was found to be unreacted.

VI

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