THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS

A Thesis

by

Else Louise Schulze

Presented to the Faculty

of the

Graduate School

of the

University of Cincinnati

in fulfillment of part of the

requirements for the degree of

Doctor of Philosophy

Cincinnati, Ohio.

June, 1926.

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS

21 D 26

ACKNOWLEDGMENT

The writer wishes to express her appreciation of the interest and advice given by Dr. H. S. Fry who suggested this investigation, and her gratitude for the fellowship stipends which were graciously granted by Dr. Ernst Twitchell, making this research possible.

It is also a pleasure to acknowledge the kindness of Mr. C. P. Long, chemist of The Globe Soap Company, who generously provided the samples of pure glycol and glycerine used in this investigation.

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS

INTRODUCTION

This research is a reinvestigation of the reactions of certain carbon compounds with fused, caustic alkalies. It differs from previous investigations in the following important respects:

(1) A new method of conducting these reactions is proposed, namely, that of passing the vapors of the carbon compounds through an equimolecular mixture of fused, caustic alkalies;

(2) A quantitative study of each reaction has been made;

(3) The reactions, so studied, have been used to illustrate and substantiate a newly proposed reaction-mechanism which involves the amphoteric dissociation of caustic alkalies; and

(4) Accordingly explains the liberation of hydrogen from carbon compounds and their concomitant oxidations ultimately to carbonates.

Each of the reactions studied has been carried out previously, but under conditions that did not yield quantitative data possessing stoichiometrical significance. A review of the chemical literature discloses numerous records of the interaction of sodium hydroxide, potassium hydroxide, soda-lime, potash-lime, and baryta with organic compounds, whereby the compounds undergo oxidation with the accompanying liberation of hydrogen. In general, the experiments performed consisted in heating a mixture of the organic substance with alkali in glass tubes, retorts, or flasks, and the data obtained, as a result of such a procedure, were far from accurate. A few of the earlier investigators, Wurtz,[1] Merz and Tibirica,[2] Hell,[3] Nef,[4,5,6] Buisine,[7] Carroll,[8] etc., obtained some quantitative results, but they are incomplete from the point of view of establishing any equations proposed to show the course and mechanism of the reactions..

In order to carry out reactions of carbon compounds with fused alkalies on a quantitative basis, a method was devised by Fry, whereby the vapors of the pure anhydrous organic compound were passed thru an equimolecular mixture of fused, anhydrous, caustic alkalies contained in an apparatus which functioned as a simple gas washing-bottle. There are no records in the chemical literature of experiments carried out under conditions identical with these, altho there are accounts of research conducted under conditions somewhat similar. A few earlier investigators, Peligot,[9] Gottlieb,[10] and Carroll,[8] vaporized the liquid compounds used before permitting them to come into contact with the alkalies, but Peligot was the only one, as far as it was possible to ascertain, who provided for complete interaction by bubbling the vapors of the carbon compound thru the fused alkalies rather than merely passing them over the surface. A variety of alkalies has been employed in previous experiments of this type, but there is no record of the use of a mixture of anhydrous sodium and potassium hydroxides, which is well adapted to such reactions because of its relatively low melting point and freedom from water (impurity). The method used in the present investigation is described in greater detail in the experimental section of this paper.

A study of the reactions of carbon compounds with alkalies led to a new interpretation of the mechanism involved. It is assumed that sodium hydroxide and potassium hydroxide are amphoteric in character, undergoing basic dissociation in aqueous medium ($NaOH \rightleftarrows Na^+ + OH^-$), and acidic dissociation in the fused state ($HONa \rightleftarrows H^+ + ONa^-$). The negative oxysodium and oxy-potassium groups, provided by the acidic dissociation of the fused alkali hydroxides, replace the negative hydrogen atoms of the carbon compound and convert the latter to one of its oxidation products. The negative hydrogen atoms from the organic compound combine with the positive hydrogen atoms supplied by the alkali and are liberated as gas. The reactions occurring are assumed to be of a general type,

$$R(H)_n + n\ HONa \longrightarrow R(ONa)_n + n\ H_2,$$

in which R is a more or less complex radical containing carbon.

HISTORICAL

In 1840, Dumas and Stas,[11] in connection with a series of experiments used as evidence for the validity of the older type theory, heated a number of organic compounds with potash lime in glass tubes, and, in each case, ascertained the products of the reactions by qualitative analysis. The results of the investigation may be tabulated as follows:

Substance	Alkali Used	Temp.	Time	Gas Products	Products in Residue
Methyl alcohol	Potash lime	-	-	hydrogen	Formate + Oxalate
Potassium formate + Oxalate	Potash lime	-	-	hydrogen	Carbonate
Cetyl Alcohol	Potash lime	210°-20°	5-6hr	hydrogen	Palmitate
Fused Oil	Potash lime	170°& up	-	hydrogen & hydrocarbon	Valerate
Glycerin	Potash lime	-	-	hydrogen	Acetate + Formate
Acetone Vapors	Potash lime	-	-	hydrogen +methane	Carbonate + traces of carbon
Acetaldehyde	Potash lime	-	-	hydrogen	Acetate
Oxalic ester	Potash lime	-	-	hydrogen	Acetate + Carbonate
Ethyl Acetate	Potash lime	-	-	hydrogen	Acetate
Benzoic ester	Potash lime	-	-	hydrogen	Benzoate + Acetate
Ethyl Iodide	Potash lime	-	-	ethylene	Iodide + Water
Ethyl Chloride	Potash lime	-	-	ethylene	Chloride + Water

Substance	Alkali Used	Temp.	Time	Gas Products	Products in Residue
Ordinary ether	Potash lime	-	-	hydrogen +methane	Carbonate
Methyl Acetate	Potash lime	-	-	hydrogen	Acetate + Formate
Methyl Chloride	Potash lime	-	-	hydrogen	Formate
Potassium formate	Potash lime	-	-	hydrogen	Carbonate
Methyl ~~ether~~	Potash lime	-	-	hydrogen	Formate
Potassium formate	Potash lime	-	-	hydrogen	Carbonate
Ethyl Alcohol	Hydrated potash	-	-	hydrogen	Acetate
Ethyl Alcohol	Anhydrous baryta	-	-	hydrogen + ethylene + trace of carbon monoxide	Acetate
Barium Acetate	Anhydrous baryta	-	-	Methane	Carbonate

In each reaction, the organic compound was converted, with the liberation of gaseous products, to the salt of the corresponding acid. Wherever brackets are used, they indicate that the residues obtained from heating the compound first mentioned were subjected to further heating and oxidized to carbonate; i.e., methyl alcohol heated with potash lime yielded, as residual products, formate and oxalate, which, in the presence of excess alkali and more heat, were converted to carbonate, with the evolution of more gas. The latter experiment verified the work of Peligot,[9] (1840), who had previously reported the decomposition of potassium formate with excess alkali to give hydrogen and oxalate, as an intermediate product, and finally hydrogen and carbonate.

In the discussion of these reactions, Dumas and Stas[11] maintained, in common with their contemporaries, that organic compounds under the influence of alkalies take over the oxygen from the water which is present and are oxidized with the liberation of hydrogen which comes jointly from the water and the carbon compound.

Pelouze and Millon,[12] engaged in similar research in 1840, studied the varying effects of anhydrous and hydrated baryta on organic compounds heated to high temperatures, and concluded that the mechanism of such reactions must be interpreted as involving the elements of water. The results of their work may be tabulated as follows:

	Substance	Alkali Used	Gaseous Products	Products in Residue
1.	Absolute alcohol	Anhydrous baryta	Methane	Barium Carbonate
2.	Methane from (1)	Hydrated baryta	Hydrogen	-
3.	Formic acid	Anhydrous baryta	Hydrogen	Barium Carbonate
4.	Anhydrous oxalates	Anhydrous baryta	Carbon Monoxide	-
5.	Anhydrous oxalates	Hydrated baryta	Hydrogen	-
6.	Carbon Monoxide	Hydrated baryta	Hydrogen	-
7.	Carbon	Hydrated baryta	Hydrogen	-

From the data obtained, the investigators formulated the following generalization: "Anhydrous baryta brings out of organic substances all the carbonic acid their composition permits them to furnish; hydrated baryta carries destruction further and tends to burn or cauterize all the carbon, while the hydrogen which is provided by the substance unites with that produced by the decomposition of water and is liberated."

The articles by Millon and Pelouze,[12] (1840), give reference to a text, entitled: "Introduction to the Study of Molecular Chemistry," wherein the author, Persoz, states that "all organic matters are decomposed with a great excess of hydrate of potash to give hydrogen." In connection with this observation, as well as in opposition to Dumas' Substitution Theory, Persoz[13] studied the reaction of hydrate of potash and acetone. Fused potassium hydroxide, contained in the curved portion of a U-tube, was submitted to the action of a stream of acetone vapor which entered at one side of the tube. The other opening of the tube was connected with vessels suitable to collect liquid and gaseous products. No distillate was collected when the acetone vapor was conducted slowly thru the alkali, but rapid passage caused large quantities of acetone to distill over unchanged. Potassium carbonate and methane, contaminated with a trace of carbon dioxide, resulted as end-products. Persoz assumed, in agreement with Dumas,[11] that the first stage of the reaction consisted in the formation of acetate, but to the second stage he attributed a more complex interpretation. He did not regard the formation of marsh gas as a simple reaction between acetate and alkali, but rather as an action of heat on acetic acid to yield acetone, which, in the presence of base, subsequently loses two volumes of carbon monoxide and assimilates two volumes of hydrogen, provided by one equivalent of decomposed water. Persoz summarized his conclusions in the following statement: "An organic substance containing carbon monoxide is able, in favorable circumstances, in the presence of water, to lose two or four volumes of carbon monoxide which are always replaced by corresponding volumes of hydrogen, provided by the decomposed water, and the oxygen of the water transforms the carbon monoxide into carbonic acid, which is freed or remains in combination."

The reaction of acetone and fused alkalies was investigated by Gottlieb[10] (1844) in his researches on the behavior of sugar in the presence of molten potassium hydroxide. Gottlieb assumed that cane sugar treated with caustic potash at high temperatures decomposes first into carbonic acid, acetone, and metacetone (an oil consisting chiefly of propionaldehyde, dimethylfurfurane, and liquid hydrocarbons). By further heating with the alkalies, the metacetone is converted, to a small extent, into propionic acid, while the acetone is simultaneously converted to formic and acetic acids, both of which are further partially oxidized to oxalic acid. In order to prove that the final products obtained resulted from the decomposition of the metacetone and acetone intermediately formed, Gottlieb carried out several subsidiary experiments. He added metacetone, drop by drop, to fused potassium hydroxide, and was able to prove the presence of small quantities of propionate in the residue, altho much metacetone distilled over unchanged. He conducted the vapors of acetone over fused caustic potash and obtained, as he had expected, a residue consisting of a mixture of potassium formate and acetate. It is probable that Gottlieb worked at temperatures low enough to prevent the decomposition of formate and acetate to give carbonate, which Dumas had reported as the sole product in the residue obtained when acetone and fused caustic interact.

Dumas'[11.] experiments on the interaction of organic compounds with potash lime at high temperatures were largely responsible for the interest aroused in that type of research among other chemists of the same period. Redtenbacher[14.] (1843) reinvestigated the interaction of glycerine with alkali, in the hope of isolating the hypothetical glycerinic acid (dihydroxy propionic acid) which Dumas and Stas had been unable to obtain, altho they believed that its formation ought to precede that of the final products - formic and acetic acids. Redtenbacher heated glycerine with solid potassium hydroxide until the mass became white, but did not glow. He failed to record the temperature of the experiment, but it was probably not over 200°C. The residue, distilled with sulphuric acid, yielded a mixture of formic and acetic acids with some acrylic acid. Redtenbacher assumed that the glycerine is converted successively into acrolein and acrylic acid. The acrylic acid decomposes to give formic and acetic acids. No trace of a glycerinic acid could be found.

Some years later, Herter[15] (1878) heated glycerine with potassium hydroxide until the mass fused. He reported that the reaction was accompanied by an evolution of hydrogen, and that the residue contained the salts of formic, acetic, butyric, and inactive lactic acids. In agreement with Redtenbacher,[14] Herter attributed the source of the acetic and formic acids to the decomposition of the intermediately formed acrylic acid. He accounted for the presence of the lactic acid by the equation:

$$C_3H_8O_3 + KOH \longrightarrow C_3H_5KO_3 + H_2O + H_2$$

The formation of the butyric acid was undoubtedly secondary, since Hoppe Seyler[16] had identified it among the products obtained when lactic acid is heated with caustic alkali.

Belohoubek[17] (1879-80) heated equimolar weights of caustic soda and glycerine at high temperatures, and obtained a distillate containing nine per cent of the theoretical yield of propylene glycol.

Fernbach[18] (1880) repeated Belohoubek's experiments and reported an eight to ten per cent yield of propylene glycol. In addition, he analyzed the remainder of the distillate and identified methyl alcohol, ethyl alcohol, isopropyl alcohol, propyl alcohol, and liquid olefines therein.

The action of soda on glycerine at high temperatures to give propylene glycol mixed with alcohols was investigated by Raisonnier[19] (1892), who identified allyl alcohol in the distillate as well as the products which Fernbach had reported.

Buisine[7] (1903) studied the reactions of glycerine with excess caustic potash in great detail, for the purpose of establishing a rapid and sensitive method for the quantitative determination of small amounts of glycerine. By a careful investigation of the products of the reaction at various temperatures, he confirmed the following four equations:

1. $C_3H_8O_3 + 2KOH \longrightarrow CH_3COOK + HCOOK + H_2O + 2H_2$ 220°-250°
2. $2C_3H_8O_3 + 4KOH \longrightarrow 2CH_3COOK + K_2C_2O_4 + 2H_2O + 5H_2$ 250°-280°
3. $2C_3H_8O_3 + 6KOH \longrightarrow 2CH_3COOK + 2K_2CO_3 + 2H_2O + 6H_2$ 280°-320°
4. $C_3H_8O_3 + 4KOH \longrightarrow 2K_2CO_3 + 3H_2 + CH_4 + H_2O$ 320°-350°

The equations show that, under the conditions of the experiment, potassium formate is stable below 250°, but decomposes above that temperature to give potassium oxalate and hydrogen ($2HCOOK \longrightarrow K_2C_2O_4 + H_2$). Above 280°, potassium oxalate is converted to carbonate and hydrogen ($K_2C_2O_4 + 2KOH \longrightarrow 2K_2CO_3 + H_2$). Above 320°, potassium acetate is oxidized in the presence of alkali to carbonate and methane ($CH_3COOK + KOH \longrightarrow K_2CO_3 + CH_4$). Buisine found that experiments which conform to the conditions prescribed by equations 3 or 4 are best for the quantitative determination of glycerine. 0.2 to 1 gram samples of glycerine introduced into a flask with excess powdered potassium hydroxide and potash lime, and heated in a mercury bath at either 320° or 350° for one hour give nearly theoretical quantities of gas required by equation 3 or equation 4, depending on the temperature used. Buisine established the stoichiometrical ratios between the weights of glycerine and the volumes of gas with quantitative data, but made no attempt to ascertain the amounts of formate, oxalate, acetate, or carbonate present at the different temperatures.

Nef[5](1904) reported that approximately equimolecular quantities of glycerine (309 grams) and pulverized sodium hydroxide (137) grams), heated to 270°-280° from six to eight hours, yielded 110 c.c. distillate, consisting primarily of methyl alcohol and small quantities of propyl and allyl alcohol, and 346 grams of residue. 310 grams of the residue were soluble in alcohol and consisted of propylene glycol , r-lactic acid (82.32 grams), traces of glycerine, and 6.3 grams of propionic acid. The salts insoluble in alcohol (36 grams) proved to be those of carbonic and oxalic acids. Hydrogen was probably evolved during the reaction, but no record of its quantity was made. It should be noted that in this experiment, as well as in those conducted by Belohoubek,[17] Fernbach,[18] and Raisonnier,[19] the temperature at which the reaction was carried out was too low and the amount of sodium hydroxide present was insufficient to permit of the complete oxidation of the glycerine to carbonate, as represented by the equation:

$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 7H_2 + 3Na_2CO_3$$

Nef found that 20 grams of glycerine, heated at 270-325° for three hours, with 60 grams of pulverized potash lime (not quite an excess) produced, with the intermediate formation of formic, oxalic, and r-lactic acids, predominantly carbonic and propionic acids and liberated 12 liters of hydrogen. Only traces of the salts of formic, oxalic, and acetic acid were found in the residue. This experiment contradicts the similar work of Buisine who, as was noted, found acetate and carbonate only in the residue obtained from the interaction of alkali and glycerine at 280-320°.

Nef[6] also investigated the action of alkalies on ethylene glycol, but, before summarizing his results, the previous work of Wurtz must be mentioned.

In 1859, Wurtz[1] found that on heating a mixture of glycol (5 grams) and potassium hydroxide (8 grams) on an oil-bath to 250°, hydrogen was evolved (4325 c.c. at 19° and 768 mm.), and the residue consisted of potassium oxalate together with small amounts of carbonate and glycollate, the quantities of which were not recorded. If the reaction proceeded in accordance with the equation:

$$C_2H_6O_2 + 2KOH \longrightarrow K_2C_2O_4 + 4H_2,$$

as Wurtz suggested, the yield of hydrogen he obtained was only about 63% of the theory (as calculated from the alkali which was not in excess.)

Nef[6] (1904) heated equimolar quantities of ethylene glycol (60 grams) and pulverized sodium hydroxide (38.7 grams) for two and one-half hours at 230-284° and obtained 25 liters of hydrogen, and 17.5 grams of distillate which contained small amounts of ethyl and methyl alcohols. The salt residue, on analysis, gave 17.4 grams of di- and some tri-ethylene glycol, glycollic acid (14 grams obtained as the calcium salt), and small quantities of formic, acetic, oxalic, and carbonic acids. Ethylene glycol, treated with excess potash lime at 250°, formed carbonate only with the liberation of hydrogen, but no record of the yields was noted.

The influence of the researches of Dumas and Stas[19] extended into the study of waxes. In 1845, Lewey[20] and Gerhardt[21] independently published accounts of an investigation of the composition of beeswax, in which they had utilized the reaction of alkalies with organic compounds to liberate hydrogen. Lewey noted that a mixture of cerine (stearic aldehyde) with potash-lime, heated in a metal-bath at 220-230°, yielded hydrogen and potassium stearate; that china wax and potash-lime gave the potassium salt of sinesique acid and hydrogen; and that cerosin gave the potassium salt of cerosic acid and hydrogen. Gerhardt verified these results and suggested the interaction of potash-lime with acids, such as pimelic, suberic, adipic, azelaic, and sebasic acids, to give hydrogen and other products as an interesting problem for investigation. He performed some experiments himself on the fusion of pimelic acid with the potassium hydroxide, and obtained hydrogen and a mixture of the salts of oxalic and valeric acids, according to the equation:

$$C_7H_{12}O_4 + 2H_2O \longrightarrow C_5H_{10}O_2 + C_2H_2O_4 + 2H_2$$

Reference to Gerhardt's work on waxes is given in Löwig's[22] text on the "Chemistry of Organic Compounds (1846). Löwig records other information on the reactions of organic compounds with alkalies at high temperatures. He states that various aldehydes, such as salicylic, cinnamic, coumarylic, and benzaldehyde are converted, by treatment with molten potassium hydroxide, to the corresponding acid, with the liberation of hydrogen. In addition, Löwig includes in his text, the results obtained by Dumas and Stas and other investigators of the time on the behavior of organic substances with fused potash, and agrees with them in their interpretation of the mechanism of the reaction, as involving the elements of water.

The study of the chemical nature of waxes was continued by B. C. Brodie[23.] (1848). Brodie converted ceryl alcohol to cerotic acid and hydrogen, by fusing it with potash-lime. Myricyl alcohol, similarly treated, yielded melissic acid and hydrogen.

The investigations of Lewey,[20.] Gerhardt,[21.] and Brodie[23.] led to the later work of Carl Hell[3.] (1884), which is more significant because of its quantitative nature. Hell proposed to determine the molecular weights of the higher alcohols by measuring the quantity of hydrogen evolved in conformity with the equation:

$$R.CH_2OH + NaOH \longrightarrow R.CO_2Na + 2H_2.$$

He heated .5 to 1 gram samples of myricyl alcohol ($C_{30}H_{61}.OH$) mixed with soda lime in hard glass tubes. The evolution of hydrogen began at 270° and ended at 290°. The gas was collected in a eudiometer over mercury, but even this precaution failed to bring the yield of hydrogen over 85%. Hell did not determine the quantity of fatty acid formed to confirm the ratio, $R.CO_2H : 2H_2$, in the general equation, nor did he extend his quantitative study to the lower alcohols, which yield volatile hydrocarbons, due to secondary decompositions that are difficult to prevent, and influence the total quantity of evolved gases. The higher alcohols may undergo these secondary decompositions also, but they yield solid hydrocarbons which do not interfere by entering the gas mixture. Since Hell was unable to obtain more than a 90% yield of hydrogen, his method was not so satisfactory in accurately determining molecular weights. The measurement of the hydrogen evolved in the presence of fused potassium hydroxide can be used, however, in distinguishing alcohols from aldehydes, and monohydric from dihydric alcohols.

Investigations, also in 1884, on the chemical constituents of Carnäubawax were conducted by Stürcke,[24.] in the manner suggested in Hell's[3.] researches. The non-acid and acid constituents obtained, after saponifying the wax in boiling alcoholic soda, were analyzed by Stürcke, and the components were identified by an examination of their reactions with soda lime. Ceryl and myricyl alcohols, together with an alcohol, $C_{25}H_{52}O_2$, of unknown structure, were found in the non-acid constituents. Ceryl alcohol, heated with soda, was converted to sodium cerotate and hydrogen, in conformity with the equation:

$$C_{27}H_{55}OH + NaOH \longrightarrow C_{26}H_{53}COONa + 2H_2$$

Myricyl alcohol, heated at 270-300° with soda-lime, yielded sodium mellisate and hydrogen, together with small quantities of carbonate and nonakosane:

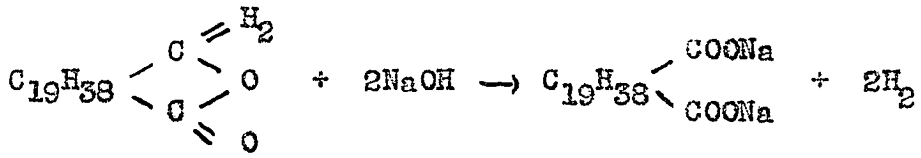
$$C_{30}H_{61}.OH + NaOH \longrightarrow C_{29}H_{59}COONa + 2H_2$$

$$C_{29}H_{59}.COONa + NaOH \longrightarrow C_{29}H_{60} + Na_2CO_3$$

Treatment of the compound, $C_{25}H_{52}O_3$, with soda-lime at 250-260° resulted in the formation of a dibasic acid, and the concomitant liberation of hydrogen. Experimental data convinced Stürcke that he was dealing with a diatomic alcohol which reacted according to the equation:

$$C_{23}H_{46}(CH_2OH)_2 + 2NaOH \longrightarrow C_{23}H_{46}(COONa)_2 + 4H_2$$

Among the acid constituents obtained from the wax, Stürcke isolated the substance $C_{21}H_{40}O_2$, which he heated with soda lime for the purpose of determining its structure. From the quantity of hydrogen evolved and the nature of the residual product, Sturcke concluded that the compound was an ester anhydride of an hydroxy acid which reacted in conformity with the equation:



Further analyses and identifications of products derived from various waxes were carried on by Schwalb[25] (1887), who also used the method of measuring the hydrogen evolved when organic compounds interact as shown by the equation:

$$R.CH_2OH + NaOH \longrightarrow R.COONa + 2H_2$$

The reactions so far considered have, in most cases, been concerned with members of those classes of substances used by Dumas and Stas[11.] in their original researches in this field. With the exception of the work of Pelouze and Millon,[12.] already noted, little investigation had been made of the interaction of carbon monoxide and alkalies before 1855. In that year, Berthelot[26.] began a series of experiments on the absorption of carbon monoxide by potash-lime, soda-lime, caustic baryta, and lime. Many of these were conducted at ordinary temperatures in the presence of small amounts of organic materials. Others were carried out at 100-220°, and, in all cases, formate was the final product. Berthelot observed that the speed of absorption rose with the temperature and quantity of alkali used. The presence of moderate quantities of water, methyl alcohol, ethyl alcohol, and ether also served to increase the velocity of absorption.

Erlenmeyer and Gütschow[27.] (1868) noted that sodium formate, obtained from the action of sodium hydroxide on carbon monoxide, gave hydrogen and carbonate, but no oxalate when further heated with excess sodium hydroxide.

The investigators probably carried out their experiments at temperatures at which oxalate is unstable and decomposes to give carbonate.

Some years later, Merz and Tibirica[1] (1877-1880) studied the reaction of carbon monoxide and fused caustic. They reported that a stream of carbon monoxide, led over soda-lime at a temperature of 200-220°, gave rapid formic acid formation, provided the carbon monoxide was moist. Above the temperature 220°, the formic acid was decomposed to give carbonate, small amounts of oxalate, and hydrogen. With caustic potash or potash-lime, this secondary decomposition took place more readily and below 220°. The investigators noted that the physical nature of the soda-lime and potash-lime has a strong influence on the binding of the carbon monoxide, and the degree of moisture and porosity plays a big role. Dry carbon monoxide was but slightly absorbed by dehydrated alkalies in comparison to the rapid absorption of the moist gas. The potash-lime reacted with carbon monoxide at a lower temperature (120°) than did the soda-lime (150°). The substitution, in the experiments, of caustic soda and potash free from lime had no influence on the initial temperature of the absorption, but caused the decomposition of formate to occur at a lower temperature. Merz and Tibirica described in detail the conditions under which they conducted their work. They recorded some quantitative data as support for their conclusions.

In connection with the study of a "New Synthesis of Carbon Acids," A. Geuther with O. Frölich and A. Looss[28.] (1880) found that finely-pulverized, anhydrous sodium hydroxide, heated in carbon monoxide at 160°, gave a large yield of formate and a small quantity of the salt of another acid richer in carbon, probably acetic acid. Geuther and his assistants postulated the following equations to show the formation of the acetic acid:

$$\begin{array}{l} 3\,CO + 4NaOH \longrightarrow 2Na_2CO_3 + H_2O + CH_2 \\ \quad CO + NaOH + CH_2 \longrightarrow NaC_2H_3O_2 \\ \hline \Sigma\ \ 4\,CO + 5NaOH \longrightarrow 2Na_2CO_3 + H_2O + NaC_2H_3O_2 \end{array}$$

Merz and Weith[29.] (1880) noted that carbon monoxide was absorbed by soda-lime at 200-220° to give sodium formate, and that moist carbon monoxide, passed over soda-lime at 300°, yielded sodium carbonate and hydrogen. They also prepared hydrogen by treating carbon monoxide with slaked lime at high temperatures. Calcium carbonate remained as the product in the residue.

A study of the carbon cell by Haber and Bruner[30.] (1904) led to further investigation of the action of fused sodium hydroxide on carbon monoxide. Their findings may be tabulated as follows:

1. Wood charcoal or graphite dissolves in boiling, concentrated, caustic sodium hydroxide with the

liberation of hydrogen.

2. Carbon is attacked by fused sodium hydroxide at 500° to give a rapid evolution of hydrogen.

3. Carbon monoxide reacts with fused sodium hydroxide at 350°, as shown by the equation:

$$2NaOH + CO \longrightarrow Na_2CO_3 + H_2$$

4. Sodium formate and sodium hydroxide, when fused together, give pure hydrogen. The reaction begins at 205° and is quite complete at 350°:

$$NaCOOH + NaOH \longrightarrow H_2 + Na_2CO_3$$

Any oxalate formed intermediately, decomposes in the presence of the alkali at 270-280°, evolving pure hydrogen and forming carbonate only:

$$Na_2C_2O_4 + 2NaOH \longrightarrow 2Na_2CO_3 + H_2$$

Following the example of Merz and Weith,[29] Vignon[31] (1911) conducted carbon monoxide over lime ($CaO.Ca(OH)_2$) at high temperatures. No sensible modification of the lime occurred below 350°. At 400°, the gaseous products consisted of a large proportion of hydrocarbons mixed with hydrogen. Above 400°, the proportion of hydrocarbons became less, and the volume of hydrogen increased. At 600° the gas collected was almost pure hydrogen. The equations occurring are the following:

$$2CO + Ca(OH)_2 \longrightarrow (HCOO)_2Ca \longrightarrow C_2O_4Ca + H_2$$

$$2(HCOO)_2Ca + CaO \longrightarrow 3CaCO_3 + CH_4$$

$$4(HCOO)_2Ca + 2CaO \longrightarrow 6CaCO_3 + C_2H_4 + 2H_2$$

Experiments consisting of heating calcium formate or oxalate alone and mixed with lime have confirmed this explanation of the origin of the hydrocarbons. Vignon showed that carbon monoxide may be converted to hydrogen and hydrocarbons to the extent of 99.5% by passage over hot lime several times, and he suggested that this might be a good way of freeing illuminating gas from this toxic constituent.

With reference to the action of carbon monoxide on lime or on sodium hydroxide or soda-lime, either dry or in the presence of water vapor, the results obtained by Levi and Piva[32.] (1916) pointed to the conclusions:

1. With pure lime, carbon monoxide gives formate at 250-300°, and carbonate and hydrogen above 300°. The formation takes place moderately slowly and to a much less extent than with sodium hydroxide. At 500-600°, the formation of hydrogen is almost quantitative, provided always that the elements of water are present.

2. The addition of sodium hydroxide to the lime facilitates the formation of formate, rendering it possible even at 150-200°, and lowers the temperature at which hydrogen is formed, the reaction proceeding in this direction to the extent of 50% at 300°. The presence of the two bases together increases the yield of hydrogen.

Reference must also be made to the work of Gianoli[33.] (1916), who prepared hydrogen from formates and from carbon monoxide.

After a study of the action of carbon monoxide on sodium hydroxide at high temperatures, Bain and Tyrrell[34.] (1917) showed that no oxalate (or only traces) is formed at temperatures between 355-490°.

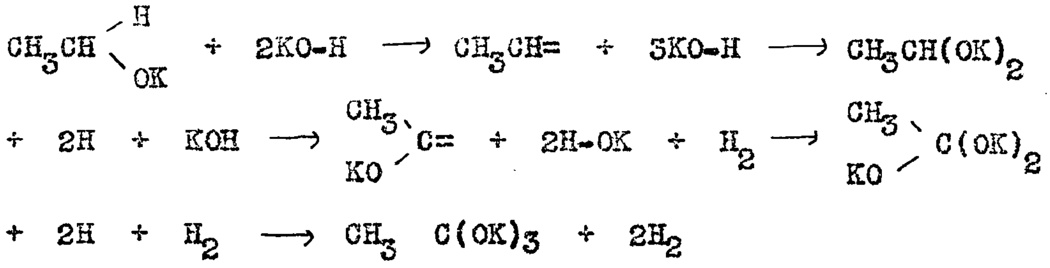
In 1918, Boswell and Dickson[35.] published an article on the interaction of organic and inorganic compounds with fused alkali. The investigators found that at 410-430°, carbon monoxide in contact with fused sodium hydroxide is oxidized to carbon dioxide, an equivalent amount of hydrogen being produced at the same time. Sodium formate, fused with caustic soda at 275°, is oxidized almost quantitatively to carbonate, with the liberation of an equivalent amount of hydrogen. Sodium oxalate is similarly oxidized at 290°. Boswell and Dickson claim that it is the water present in the fusion, catalyzed by the sodium hydroxide, which is the effective oxidizing agent.

Boswell and Dickson extended the application of the fusion reactions to the phenols and sulphonic acids. Among other experiments, the investigators heated .5 gram of resorcinol with 2 grams of sodium hydroxide for forty-five minutes at 350°, and obtained only .4 c.c. of hydrogen and .1 c.c. of methane. They concluded that "resorcinol[36.] does not take part in this general reaction and does not give off hydrogen until it has first absorbed atmospheric oxygen, and has thus presumably been oxidized to some compound which does take part in the general reaction."

The methods of treating alcohols with fused alkalies, as inaugurated by Hell,[3.] were used by Nef[4.] (1901) in applying his dissociation theory to the monatomic alcohols, and their metallic derivatives. In a number of isolated experiments on known quantities of such substances as isoamyl alcohol, tertiary amyl alcohol, sodium isoamylate, sodium salt of tertiary amyl alcohol, sodium isobutylate, etc., with known quantities of potash-lime or soda-lime at different temperatures, ranging between 170-450°, Nef obtained definite amounts of hydrogen, and salts of the corresponding acids. In some cases, when the higher temperatures were used, the products were mixed with methane and carbonate. He gives quantitative data, and his results in general substantiate the equation:

$R.COH + M.OH \rightarrow R.COOM + H_2$, although some secondary actions may occur. Nef did not find any olefines in his gas mixtures, nor did he note the presence of hydrocarbons other than methane although the salts of some of the acids obtained might be expected to yield higher hydrocarbons on decomposition with sodium hydroxide. The methane formation, in each case, occurs, according to Nef, as the result of the union of CH_2 particles with H particles formed intermediately.

The behavior of ethyl alcohol at 250° with excess caustic potassium hydroxide to give hydrogen and potassium acetate quantitatively is explained, by Nef,[4] as occurring through alkylidene dissociation:



$$CH_3CH\begin{matrix}H\\OK\end{matrix} + 2KO\text{-}H \longrightarrow CH_3CH= + 3KO\text{-}H \longrightarrow CH_3CH(OK)_2$$

$$+ 2H + KOH \longrightarrow \begin{matrix}CH_3\\KO\end{matrix}C= + 2H\text{-}OK + H_2 \longrightarrow \begin{matrix}CH_3\\KO\end{matrix}C(OK)_2$$

$$+ 2H + H_2 \longrightarrow CH_3\ C(OK)_3 + 2H_2$$

Nef does not record the presence of any ethylene in the reaction products.

B. H. Carroll[8] (1918) carried out a quantitative investigation of the action of the vapors of absolute ethyl alcohol and of acetaldehyde on soda-lime. Carroll states that soda-lime was used instead of sodium hydroxide, which is liquid at high temperatures and difficult to handle. In the experiments with alcohol, the two reactions:

(1) $CH_3CH_2OH + NaOH \longrightarrow CH_3CO_2Na + 2H_2$

(2) $CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4$

occur at 250°, but the velocity of reaction (2) is not enough to decompose the acetate as fast as it is formed, until the temperature reaches 450°. Carroll's data on hydrogen, methane, and acetate determinations substantiate equations (1) and (2) to a limited extent, but, in no instances, did he indicate the quantity of carbonate formed, which is equally as important as the acetate. About 10% of the alcohol takes place in side reactions giving aldehyde tars, ethylene, methane, and carbon monoxide from the decomposition of the intermediately formed acetaldehyde. Some alcohol distills over unchanged. According to Carroll, an increase in the rate of feed cuts down the per cent of alcohol decomposed, while too great a decrease in the rate of feed seems to make secondary reactions more important.

Carroll states that the conversion of alcohol to acetate, in the presence of soda-lime, takes place in three stages. The first stage consists of the dissociation of alcohol to aldehyde and hydrogen, in the presence of caustic soda as catalytic agent:

(1) $CH_3CH_2OH + NaOH \longrightarrow CH_3CHO + NaOH + H_2$

Aldehyde is found in the liquid products, if sodium hydroxide is used, while, if soda-lime is used, aldehyde tar is formed.

The second stage consists of the decomposition of acetaldehyde to give ketene and hydrogen, in the presence of sodium hydroxide as catalytic agent:

(2) $CH_3CHO + NaOH \longrightarrow CH_2CO + NaOH + H_2$

Carroll did not prove the intermediate formation of ketene, but he believed that it would be the normal product in such a case of dehydrogenation.

The third stage in the reaction is the combination of ketene with caustic soda to form sodium acetate:

$$(3)\ CH_2CO + NaOH \longrightarrow CH_3COONa$$

Experiments with acetaldehyde and sodium hydroxide showed that the reaction begins at 300° and is quantitative at about 450°. The equations are:

$$CH_3CHO + NaOH \longrightarrow CH_2CO + NaOH + H_2$$

$$CH_2CO + NaOH \longrightarrow CH_3CO_2Na$$

$$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$$

As in the case of the alcohol reaction, no quantitative data on carbonate determinations were recorded.

Weitkamp[37] (1923) carried out a number of experiments on the fusion of organic compounds with alkalies. She found that it was not possible to alter benzene by passing it thru fused sodium and potassium hydroxides, probably because of the difficulty of replacing the initial hydrogen atom of the carbon in the nucleus, nor would ethylene undergo any reaction in the presence of the alkalies. Weitkamp noted that acetylene passed thru fused alkalies gave hydrogen and a residue consisting not of acetate, as Feuchter[38] had claimed, but of carbonate. The reactions occurring were:

$$H\text{-}C \equiv C\text{-}H + 2NaOH \longrightarrow CH_3CH(ONa) \qquad \text{(Feuchter)}$$

$$CH_3CH(ONa)_2 + HONa \longrightarrow CH_3C(ONa)_3 + H_2$$

Methyl alcohol also interacted with sodium and potassium hydroxides at high temperatures and gave hydrogen, carbon monoxide and carbonate, presumably in agreement with the equation:

$$2CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + CO + 5H_2$$

In each of the cases mentioned, the mechanism of the reactions follows that of a general type reaction:

$$R(H)_n + n(HOM) \longrightarrow R(OM)_n + n\ H_2$$

(where M = Na or K), and from all indications the alkali hydroxides act amphoterically, ionizing both as bases and as acids.

In 1924, Fry, Schulze, and Weitkamp[39.] reported that experiments with formaldehyde and methyl alcohol and fused, dehydrated, caustic sodium hydroxide and potassium hydroxide in equimolar mixtures, carried out on a quantitative basis, as fully as the type of apparatus would permit, confirmed the two following reactions:

$$HCOH + 2NaOH \xrightarrow{260°-300°} Na_2CO_3 + 2H_2$$

$$CH_3OH + 2NaOH \xrightarrow{300°-325°} Na_2CO_3 + 3H_2$$

which are in agreement with the general type reaction proposed:

$$R(H)_n + n\ HONa \longrightarrow R(ONa)_n + n\ H_2$$

Experiments with acetylene led to the conclusion that carbonate, not acetate, results as the final oxidation product, when the unsaturated gas interacts with fused sodium and potassium hydroxides, and that the gases produced consist of a mixture of methane and hydrogen. The reaction which probably occurs is:

$$C_2H_2 + 4NaOH \xrightarrow{300°-325°} C(ONa)_4 + H_2 + CH_4$$

In addition, Fry and Schulze[40.] (1924) found that experiments with ethyl alcohol and fused, dehydrated caustic alkalies at 300-325° yielded hydrogen, methane, and carbonate in quantities that apparently substantiated the equation:

$$C_2H_5OH + 2NaOH \longrightarrow Na_2CO_3 + CH_4 + 2H_2$$

Some ethylene was found in the gas mixtures as a result of the decomposition:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

The amphoteric and oxidizing properties of sodium hydroxide are well illustrated in these reactions by the substitution of oxysodium groups for hydrogen atoms in the compound, and by the formation of carbonate in each case.

THEORETICAL

In the majority of the cases cited in the historical development of alkali fusions with organic compounds at high temperatures, the mechanism of the reactions may be shown to conform to the proposed type equation:

$$R(H)_n + n\ H(OM) \longrightarrow R(OM)_n + n\ H_2$$

(where M = Na or K). From all indications, the alkali hydroxides act amphoterically, ionizing both as bases ($NaOH \rightleftarrows \overset{+}{Na} + \overset{-}{OH}$) and as acids ($HONa \rightleftarrows \overset{+}{H} + \overset{-}{ONa}$). Just as acids in the concentrated state have been known to dissociate basically,[41.]

$$(HNO_3 \rightleftarrows \overset{+}{NO_2} + \overset{-}{OH})$$

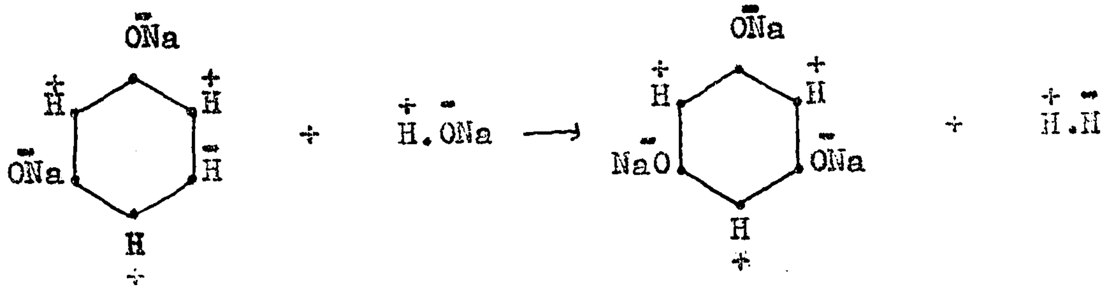
$$(H_2SO_4 \rightleftarrows \overset{++}{SO_2} + 2\ \overset{-}{OH})$$

so, in the fused state, the concentrated alkali hydroxides undergo acidic dissociation especially, and function as oxidizing agents according to the proposed type reaction noted. The hydrogen atoms of the carbon compounds at high temperatures are very likely negative, since they are replaced by negative oxysodium or oxypotassium groups, with the formation of salts of a higher state of oxidation than the original compound. The fact that the electrolysis of hydrides, such as lithium[42.] and calcium hydride[43.] results in the liberation of hydrogen at the anode, confirms the assumption that hydrogen may bear either a negative charge or a positive charge, as originally postulated by Fry,[44] and, according to Lewis[45] "may from time to time become polarized in one direction or the other, as a consequence of disturbance due to thermal motion." The hydrolysis of lithium hydride on the one hand and the interaction of a carbon compound with sodium hydroxide on the other may be represented by polar formulas as parallel reactions:

$$\mathrm{Li^{+}H^{-}} \quad + \quad \overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}} \longrightarrow \overset{+}{\mathrm{Li}}\ \overset{-}{\mathrm{OH}} \quad + \quad \overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{H}}$$

$$\mathrm{R^{+}\ H^{-}} \quad + \quad \overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{ONa}} \longrightarrow \overset{+}{\mathrm{R}}\ \overset{-}{\mathrm{ONa}} \quad + \quad \overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{H}}$$

The acid dissociation and oxidizing action of sodium hydroxide with the concomitant liberation of hydrogen is exemplified in the conversion of resorcinol into phloroglucinol on fusion with alkali:



This reaction is of theoretical importance, since it illustrates the necessity of assuming not only the amphoteric character of sodium hydroxide, but the possibility of negative hydrogen in carbon compounds. It also illustrates and confirms the electronic polar valence formula of benzene proposed by Fry.[46]

OBJECT OF INVESTIGATION

The object of this investigation is fourfold:

1. To bring about the reaction of
   - A. Ethyl Alcohol
   - B. Acetaldehyde
   - C. Acetone
   - D. Resorcinol
   - E. Carbon Monoxide
   - F. Glycol
   - G. Glycerine

with the fused alkalies, under conditions favorable for the complete contact of the interactants and the collection of the resulting products. This necessitated the development of a new mode of experimentation applicable generally to each compound investigated.

2. To carry out a quantitative analysis of the products formed, in the attempt to substantiate the stoichiometrical ratios between the gas volumes and the weights of compounds used and formed, as required by the equations which are proposed to account for the course of the reactions.

3. To study the course of the reactions at different temperatures, noting particularly the formation of intermediate oxidation products which are predicted by the steps involved in the application of the type reactions.

4. To show that the results obtained in these experiments verify quantitatively the equations proposed

for ethyl alcohol, acetaldehyde, acetone, resorcinol, carbon monoxide, glycol, and glycerine, which follow a priori from the application of the type reaction mechanism, and are evidence for its validity and value in correlating known facts and predicting new ones.

APPARATUS AND METHOD

The apparatus used in all experiments consisted of an outer iron tube, 30 cm. long and 5 cm. in diameter, threaded at both ends, closed at the bottom with a cap, and at the top with a reducing coupling thru which passed, tightly screwed, a long, narrow, inner tube, 40 cm. in length and 2.5 cm. in diameter, extending to within .5 cm. of the bottom of the outer tube. The vapors of the carbon compounds experimented upon were conducted, thru the inner tube, into an equimolecular mixture of sodium hydroxide and potassium hydroxide (previously dehydrated by fusion at red heat and analyzed for carbon dioxide content) contained in the outer tube. The gases evolved passed thru an inclined side neck, 20 cm. long and 1 cm. in diameter, fitted in the outer tube, 9 cm. below the reducing coupling, and thence into a Liebig condenser and safety bottle (immersed in a freezing mixture to condense any liquefiable products, and were collected over water in bottles of graduated capacity. The apparatus functioned as a simple gas washing-bottle, that is, the vapors of the carbon compounds under investigation were bubbled thru the fused alkalies. The lower end of the outer iron tube was submerged 9 cm. in a solder bath. Temperature readings were supplied by a thermometer, immersed in the solder bath, unless temperatures above 350° were used, in which case a Brown pyrometer was employed.

Analyses of the residue for carbon dioxide were made by alkalimeter determinations. The quantities of carbon dioxide present in the original alkalies were also determined, and deducted from the total amounts found in the residue.

Acetate was determined by liberation as acetic acid and titration with standard sodium hydroxide solution, as described by Scott - "Standard Methods of Chemical Analysis", Volume II (1922), page 1057.

The gases were analyzed by the absorption and explosion methods of Hempel, and the volumes were calculated to standard conditions in all data recorded.

EXPERIMENTAL PART

A. Ethyl Alcohol

Ethyl alcohol vapor was brought into interaction with an equimolar mixture of fused sodium and potassium hydroxides by attaching a Walter dropping-funnel, containing 50 c.c. of ethyl alcohol and equipped with an equalizing pressure device, to the upper end of the inner iron tube of the apparatus previously described. The stem of the dropping funnel, passing thru a tightly fitting rubber stopper, was bent sufficiently to permit the escaping drops of alcohol to impinge upon and flow down the inner wall of the hot iron tube and thus cause a steady flow of alcohol vapor to pass thru the fused alkalies, which were maintained at a temperature of 250-280°C. About 30 c.c. of distillate was collected, most of which consisted of undecomposed alcohol. The exact quantity of ethyl alcohol entering into the reaction could not be determined.

The gases collected were analyzed and found to consist of hydrogen, methane, and ethylene, the total quantities of each of which were determined.

The reaction residue contained acetates and carbonates, the total amounts of which were determined as acetic acid and carbon dioxide respectively.

In extending the type reaction:

$$R(H)_n + n\,H(OM) \longrightarrow R(OM)_n + n\,H_2$$

to ethyl alcohol, the hydrogen atoms of the CH_2OH radical would naturally be the first susceptible to replacement, and the oxidation to aldehyde may be shown to occur as follows:

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2O \qquad (1)$$

$$CH_3CH_2ONa + HONa \longrightarrow CH_3CH(ONa)_2 + H_2 \qquad (2)$$

$$CH_3CH(ONa)_2 + H_2O \longrightarrow CH_3CHO + 2NaOH \qquad (3)$$

$$\sum 1, 2, 3. \qquad CH_3CH_2OH \longrightarrow CH_3CHO + H_2 \qquad (4)$$

Carroll[8/] reported that slight traces of aldehyde were noticeable in the reaction between alcohol and caustic soda. The aldehyde undergoes further oxidation to sodium acetate, in conformity to the type reaction:

$$CH_3CHO + HONa \longrightarrow CH_3CO(ONa) + H_2 \qquad (5)$$

Reactions 4 and 5 together, indicate the oxidation of alcohol to acetate:

$$\sum 4, 5. \qquad CH_3CH_2OH + HONa \longrightarrow CH_3COONa + 2H_2 \qquad (6)$$

The further conversion of sodium acetate to carbonate, with the liberation of methane, may then follow, according to the reaction:

$$CH_3COONa + HONa \longrightarrow Na_2CO_3 + CH_4 \qquad (7)$$

Reaction 7, however, does not occur to any great extent, unless the temperature is raised above 250°.

The use of the type reaction to explain the mechanism of the changes occurring when alcohol interacts with alkalies makes Carroll's[8] assumption of the intermediate formation of ketene unnecessary. In fact, Carroll has stated that "the intermediate formation of ketene has not been shown."

If the type reaction should also involve the hydrogen atoms of the methyl radical of ethyl alcohol, complete oxidation to carbonate and orthocarbonate is quite conceivable in terms of the following reaction:

$$CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2 \quad ? \quad (8)$$

Reaction 8 will serve to explain the excessive yield of hydrogen formed over that required by the theory according to equation 6.

The ethylene found in the gas mixtures was likely due to the catalytic decomposition of ethyl alcohol at the temperatures used:

$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \qquad (9)$$

Since the total quantities of ethyl alcohol entering into the reactions were not definitely known (because of the distillation of undecomposed alcohol with other liquefiable products), no calculations could be made, based on the amounts of alcohol used. Besides, reactions 6, 7, 8, and 9 are simultaneous and independent, so it was not possible to obtain quantitative data completely establishing the stoichiometrical ratios between yields of acetate, carbonate, hydrogen, and ethylene. Nevertheless, the data given in Table I, which summarize the analytical results of two runs, substantiates in some measure the type reactions noted. The per cent theoretical of hydrogen is based on the amount of acetate formed according to equation 6, in terms of the stoichiometrical ratio $CH_3CO_2H : 2H_2$. The per cent theoretical yield of methane is based on the carbonate formed in equation 7 and its ratio $CO_2 : CH_4$. The per cent theoretical yield of ethylene formed according to equation 9 could not be calculated, since no corresponding product occurs in the residue.

Table I

Run	CH_3CO_2H Found G.	H_2(L. 0/760) Found	H_2(L. 0/760) Calculated	Per cent Calculated
I	7.40	6.16	5.53	111.40
II	3.49	2.71	2.61	103.83
	CO_2 (G.) Found	CH_4(L.0/760) Found	CH_4(L.0/760) Calculated	Per cent Calculated
I	1.17	0.086	0.596	14.43
II	1.37	0.030	0.699	4.30
	C_2H_4(L.0/760) Found			
I	3.37			
II	3.88			

Examination of the table shows that the volume of hydrogen found, as compared with that calculated from the acetate, is over 100% in each run. This may be due to the fact that the total acetate was not known, since some of it had undergone further oxidation to carbonate, and, therefore, the hydrogen value as calculated from it would necessarily be lower than the practical yield. On the other hand, the occurrence of equation 8 would also account for excessive yields of hydrogen.

The volumes of methane obtained were much smaller than would be expected from the weights of carbon dioxide found. Either much methane was lost by solution in the large quantities of water present during the collection of the gases, or excess carbon dioxide was formed as the result of the occurrence of equation 8.

The large quantities of ethylene obtained show the extensive occurrence of equation 9.

B. Acetaldehyde

Since acetaldehyde probably occurs as an intermediate product in the oxidation of ethyl alcohol by alkalies, an investigation of its reaction with sodium and potassium hydroxides was undertaken in the hope of further substantiating equations 5 and 7.

Vapors of pure acetaldehyde were bubbled thru the equimolar mixture of fused caustic alkalies at three different temperatures. In each case the acetaldehyde reacted completely and no distillate was collected. Runs were made at 250°, 300°, and 350° and the reaction products were analyzed quantitatively. The gases were mixtures of hydrogen and methane, and the proportion of methane to hydrogen was higher at the higher temperatures. The reaction residue consisted of acetate and carbonate in the 250° run, and of carbonate alone in the 300° and 350° runs.

The course of the reaction may be indicated in equations 5 and 7, and in their summation, equation 10, as follows:

$$CH_3CHO + HONa \longrightarrow CH_3CO(ONa) + H_2 \qquad (5)$$

$$CH_3COONa + HONa \longrightarrow Na_2CO_3 + CH_4 \qquad (7)$$

$$\sum 5, 7. \quad CH_3CHO + 2NaOH \longrightarrow Na_2CO_3 + H_2 + CH_4 \qquad (10$$

The temperature of the experiment determined the extent to which reactions 5, 7, 10 took place. The data from three runs are summarized in Table II.

Table II

Acetaldehyde: I (250°); II (300°); III (350°)

Run	CH_3CHO (G.)	H_2 (L. 0/760) Found	H_2 (L. 0/760) Theory	Per cent Theory
I	15.75	7.44	8.02	92.71
II	15.35	7.36	7.82	94.12
III	15.75	8.05	8.02	100.31

	CH_3CHO (G.)	CH_4 (L. 0/760) Found	CH_4 (L. 0/760) Theory	Per cent Theory
I	15.75	0.26	8.02	3.25
II	15.35	7.55	7.82	96.55
III	15.75	7.41	8.02	92.40

	CH_3CHO (G.)	CO_2 (G.) Found	CO_2 (G.) Theory	Per cent Theory
I	15.75	1.00	15.75	6.35
II	15.35	15.77	15.35	102.74
III	15.75	13.66	15.75	86.73

	CH_3CHO (G.)	CH_3CO_2H (G.) Found	CH_3CO_2H (G.) Theory	Per cent Theory
I	15.75	20.37	21.4	95.19
II	15.35	---	---	---
III	15.75	---	---	---

In run I, acetaldehyde interacted completely with excess of caustic alkali at 250°, and gave more than 90% yields of hydrogen and acetates. Therefore, the reaction conformed, within the limits of experimental conditions, to the stoichiometrical ratios required by equation 5:

$$CH_3CHO + HONa \longrightarrow CH_3CO(ONa) + H_2 \qquad (5)$$

Since very small yields of methane and corresponding carbonates were obtained, reaction 7 took place to a limited extent:

$$CH_3COONa + HONa \longrightarrow Na_2CO_3 + CH_4 \qquad (7)$$

In runs II and III at 300° and 350° respectively, the yields of hydrogen, methane, and carbonate are practically theoretical for the summation of reactions 5 and 7; namely, reaction 10:

$$CH_3CHO + 2NaOH \longrightarrow Na_2CO_3 + H_2 + CH_4 \qquad (10)$$

The carbon dioxide yield in run III at 350° was somewhat low (86.73%) probably due to the difficulty encountered in attempting to remove all of the residue from the iron tube in which the reaction took place.

C. Acetone

The quantitative study of the behavior of acetone toward fused alkalies naturally follows from that of acetaldehyde, since the two compounds are structurally similar. It is logical to assume that its interaction with fused caustic would conform to the preceding type reactions 5, 7, and 10, shown by acetaldehyde. Analogously the type reactions for acetone , 11, 7, and 12, the latter being the summation of the two preceding, are:

$CH_3COCH_3 + NaOH \longrightarrow CH_3CO_2Na + CH_4$ (11)

$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$ (7)

$CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$ (12)

Two sets of experiments were conducted to check these assumptions and reactions quantitatively. Twenty gram samples of pure acetone were passed, as vapor, thru the equimolar mixture of fused alkalies at a temperature of 250° in Run I and at 350° in Run II.

At 250°, methane was the principal gas evolved with small amounts of hydrogen and unsaturated hydrocarbons, and traces of carbon monoxide. The reaction residue was chiefly acetates and small quantities of carbonates.

In run II at 350°, the yield of methane was more than doubled. It contained little hydrogen, no unsaturated hydrocarbon, and no carbon monoxide. The reaction residue was chiefly carbonates with no acetates.

The quantitative data of both runs are summarized in Table III, which, for purposes of comparison, indicates theoretical yields and per cent theoretical yields calculated on the basis of equations 11 and 12. Since only a few drops of liquid possessing the characteristic odor of acetone condensation products were collected, as distillate, in each run, all calculations were based on the original amounts of acetone used.

Table III

Acetone: I (250°); II (350°)

Run	$(CH_3)_2CO$ (G.)	CH_4(L.0/760) Found	CH_4(L. 0/760) Theory Equation (11)	CH_4(L. 0/760) Per cent Theory Equation (11)	CH_4(L.0/760) Theory Equation(12)	CH_4(L.0/76 Per cent Theory Equation(1
I	19.75	5.41	7.63	70.91	15.26	35.46
II	19.98	14.27	---	---	15.44	92.43

	$(CH_3)_2CO$ (G.)	CH_3CO_2H(G.) Found	CH_3CO_2H(G.) Theory Equation (11)	CH_3CO_2H Per cent Theory Equation (11)
I	19.75	17.33	20.44	84.79
II	19.98	none	none	none

	$(CH_3)_2CO$ (G.)	CO_2(G.) Found	CO_2(G.) Theory	CO_2 Per cent Theory
I	19.75	3.32	14.99	22.15
II	19.98	13.94	15.16	91.96

In drawing conclusions from the above data, it should be noted that yields of methane may originate in reaction 11 or 7, or in their summation reaction 12. In run I, however, the 84.79% yield of acetate and corresponding but somewhat lower 70.91% yield of methane are fairly commensurate with the stoichiometrical ratio,

CH_3CO_2H : CH_4 , required by equation 11. The solubility of methane in water, large volumes of which were present during the collection of the gases, may explain its lower yield in comparison to the acetate yield. The data indicate that at 250° at least 70% of the acetone used reacted with alkalies according to reaction 11.

In run II, the 91.96% yield of carbonates (calculated as carbon dioxide) and corresponding 92.43% yield of methane substantiate the stoichiometrical ratio, CO_2 : $2CH_4$, required by equation 12. At least 90% of the acetone used, therefore, reacted with the fused alkalies at 350° in conformity with reaction 12:

$$CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4 \qquad (12)$$

The small quantities of hydrogen, unsaturated hydrocarbons, and carbon monoxide found in the gas mixtures in run I indicate that side reactions occurred to a slight extent. The production of hydrogen, which was obtained in run I and II, may be explained as having resulted from the complete oxidation of a small amount of the acetone to carbonate and orthocarbonate, as represented by the type reaction 13, involving the hydrogen atoms of the methyl radicals:

$$CH_3COCH_3 + 10NaOH \longrightarrow Na_2CO_3 + 2Na_4CO_4 + 8H_2 \qquad (13)$$

This is analogous to equation 8 under ethyl alcohol:

$$CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2 \qquad (8)$$

which served to explain the excess yield of hydrogen over that required by equation 6.

D. Resorcinol

Experiments with resorcinol were undertaken as a result of a recent article by Boswell and Dickson[36] in which the authors state that resorcinol does not take part in the general reaction of organic compounds with fused alkalies and "does not give off hydrogen until it has first absorbed atmospheric oxygen and has thus persumably been oxidized to some compound which does take part in the general reaction." They reported that .5 gram of resorcinol[35] heated with 2 grams of sodium hydroxide for forty minutes at 350° yielded only 0.4 c.c. of hydrogen and 0.1 c.c. of methane.

For the purpose of either substantiating these results or of showing that the dihydroxy aromatic compound does react with fused caustic in accordance with the type reaction, 0.55 gram of resorcinol (1/200 mol) was heated with 2 grams of an equimolar mixture of sodium and potassium hydroxides in a tube which had previously been filled with hydrogen to prevent any access to oxygen. The evolution of hydrogen began at 420° and ceased at 490° after seven hours heating. The total volume of gas collected (at 0°/760 mm.) was 598 c.c., of which 407 c.c.

were hydrogen. This yield of hydrogen was 90.85% of the theory for all the available hydrogen of resorcinol according to the type reaction:

$$C_{\cancel{4}6}H_4(OH)_2 + 6MOH \longrightarrow C_6(OM)_6 + 2H_2O + 4H_2$$

The reaction residue was not identified as $C_6(OM)_6$, but chiefly as decomposition products, i.e., alkali carbonates and free carbon. Alkalimeter determinations gave .5406 grams of carbon dioxide, which is 40.96% of the theory for all the carbon in resorcinol. So it is quite evident that higher and longer heating of resorcinol with mixed alkalies gives almost theoretical yields of hydrogen, the evolution of which is not dependent, as Boswell and Dickson maintain, on previous heating with access to oxygen.

E. Carbon Monoxide

The two investigators, Boswell and Dickson,[35] who were mentioned in connection with reactions on resorcinol, have reported experiments on the reactions of various substances with fused alkalies as oxidizing agents, and have maintained, in common with Dumas and Stas,[11] that the mechanism of these reactions consists ultimately in the decomposition of water, the oxygen carrying the compound under investigation to a higher state of oxidation and the hydrogen being evolved in the gaseous state. Some such reactions may virtually involve the decomposition of water, but the writer is more strongly inclined to the hypothesis, advanced by Fry, that the mechanism of these reactions involves primarily the acidic dissociation of the alkali hydroxides and conforms to the type reaction. For this reason, not only the alkalies, but all compounds used in the experiments have been carefully dehydrated to eliminate, as far as possible, the presence of any water during the reaction. Of course, in many cases, water is formed during the course of the reaction, and so a compound which would not be likely to provide water in its interaction with fused caustic and which would show that the presence of water is not necessary to the oxidation of a carbon compound with liberation of hydrogen, was chosen for investigation.

The reactions which would occur if carbon monoxide reacts according to the type equation are:

$$CO + NaOH \longrightarrow HCOONa$$

$$HCOONa + NaOH \longrightarrow Na_2CO_3 + H_2$$

Co + [illegible]

Carbon monoxide, prepared by the interaction of potassium ferrocyanide and concentrated sulphuric acid, and passed thru potassium hydroxide solution, concentrated sulphuric acid, and phosphorus pentoxide to remove carbon dioxide, sulphur dioxide, and water, was bubbled thru the equimolar mixture of fused alkalies at a rate of one liter in one-half hour at two different temperatures - run I at 250° and runs II and III at 350°.

In run I at 250°, the gases collected consisted of approximately one-half carbon monoxide and one-half hydrogen by volume. The residues were chiefly carbonates with traces of formates. There was no distillate.

In runs II and III at 350°, the volumes of hydrogen in the gas mixtures were much higher (about 75-85%) with about 15-25% of carbon monoxide. The reaction residue contained carbonate which checked the hydrogen value in the ratio, $CO_2 \div H_2$, over 90%. An infinitessimal amount of moisture appeared in the condenser during the reaction. Its source was not determined.

The analytical data from three runs are summarized in Table IV:

Table IV

Carbon Monoxide: I (250°); II and III (350°)

Run	CO (L.0/760) Volume used	CO (L.0/760) In gases	H_2 (L.0/760) In gases	CO_2 (G.) Found	H_2 (L.0/760) Theory Based on CO_2	H_2 Per cent and Theory Based on CO_2
I	7.7	4.04	3.32	7.37	3.76	88.30
II	9.3	2.23	6.87	14.8	7.54	91.12
III	8.75	0.926	7.55	16.35	8.33	90.64

The slightly low yield of hydrogen in run I, calculated on the basis of the ratio, $CO_2 : H_2$, was probably due to the fact that all of the formate had not decomposed at the lower temperature. Traces of formate found in the reaction product verified this assumption.

At 250°, less of the carbon monoxide was absorbed (50%) than at 350° (75 - 85%), but, at both temperatures, the residues were largely carbonates, showing that any formate intermediately formed had been entirely oxidized to the carbonate stage, with the liberation of an equivalent amount of hydrogen. These results bear out the observations of Merz and Tibirica[1] who had reported that sodium formate and soda lime react to give carbonate and hydrogen at 220°, while potassium formate, in the presence of potash lime, similarly decomposes below that temperature.

Merz and Tibirica had stated that dry carbon monoxide was but slightly absorbed by dehydrated alkalies, the presence of water being necessary to the course of the reaction. Water may cause a more complete and greater velocity of reaction between carbon monoxide and caustic alkali, but the above data indicates that the reaction does occur in its absence.

The conclusion of Boswell and Dickson[35] that it is the water present in the fusion, catalyzed by the sodium hydroxide, which is the effective oxidizing agent, is likewise contradicted by the data in Table IV.

F. Ethylene Glycol

The application of the type reaction to glycol gives a series of partial equations which may be summarized as follows:

$$CH_2OH.CH_2OH + 2NaOH \longrightarrow CH_2ONa.CH_2ONa + 2H_2O \tag{1}$$

$$CH_2ONa.CH_2ONa + 4HONa \longrightarrow C(ONa)_3.C(ONa)_3 + 4H_2 \tag{2}$$

$$C(ONa)_3.C(ONa)_3 + 2H_2O \longrightarrow CO_2Na.CO_2Na + 4NaOH \tag{3}$$

$$\sum 1,2,3. \quad CH_2OH.CH_2OH + 2NaOH \longrightarrow CO_2Na.CO_2Na + 4H_2 \tag{4}$$

Equation 4, the summation of 1, 2, 3, affords an explanation of the mechanism of the oxidation of glycol to oxalic acid. The oxalic acid undergoes further type reaction as follows:

$$CO_2Na.CO_2Na + NaOH \longrightarrow HCO_2Na + Na_2CO_3 \tag{5}$$

$$HCO_2Na + NaOH \longrightarrow Na_2CO_3 + H_2 \tag{6}$$

$$\sum 4,5,6. \quad CH_2OH.CH_2OH + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \tag{7}$$

Equation 7, the summation of 4, 5, 6, indicates the mechanism of the oxidation of glycol to carbonate, with the accompanying liberation of hydrogen.

It is also possible to apply the type reaction to glycol, whereby one CH_2OH group is oxidized entirely before the other is attacked. In this case, glycollic acid is formed as an intermediate product as follows:

$$CH_2OH.CH_2OH + NaOH \longrightarrow CH_2OH.CH_2ONa + H_2O \tag{8}$$

$$CH_2OH.CH_2ONa + 2HONa \longrightarrow CH_2OH.C(ONa)_3 + 2H_2 \tag{9}$$

$$CH_2OH.C(ONa)_3 + H_2O \longrightarrow CH_2OH.CO_2Na + 2NaOH \qquad (10)$$

$$\sum 8,9,10. \quad CH_2OH.CH_2OH + NaOH \longrightarrow CH_2OH.CO_2Na + 2H_2 \qquad (11)$$

Equation 11, the summation of 8, 9, and 10, indicates the oxidation of glycol to glycollic acid, which then undergoes further change:

$$CH_2OH.CO_2Na + 3NaOH \longrightarrow 2Na_2CO_3 + 3H_2 \qquad (12)$$

$$\sum 11,12. \quad CH_2OH.CH_2OH + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (13)$$

Equation 13, the summation of 11 and 12, is identical with equation 7. If, therefore, it is assumed that the type reaction can be applied to the dihydroxy alcohol, then the final results of the complete oxidation of glycol to carbonate should conform to the stoichiometrical ratios demanded by equation 13, regardless of the intermediate steps by which it was reached.

In order to establish these stoichiometrical ratios, $(CH_2OH)_2:5H_2$, $(CH_2OH)_2:2CO_2$, and $2CO_2:5H_2$, experiments with glycol and fused caustic alkalies were carried out.

The glycol, supplied by the courtesy of The Globe Soap Company, and purified by distillation until it boiled correctly at 197.5°, was added slowly over a period of 4 hours from the Walter dropping-funnel to the equimolar mixture of fused, dehydrated sodium and potassium hydroxides. 10 c.c. portions were used in runs conducted at 250° and at 350°.

In Run I, at 250-260°, the gas evolution ceased after 28 hours heating. No distillate was collected. The gas mixture contained hydrogen with traces of methane. The residue consisted almost entirely of the hydroxides and carbonates of sodium and potassium, altho oxalates were present in very small quantities (equivalent to about 0.5 gram oxalic acid).

In Runs II and III, at 345-355°, the gas evolution ceased after 5-7 hours heating. Toward the end of each run, a trace of distillate, having a peculiar, aromatic odor, appeared in quantities too small to be either weighed accurately or analyzed. The gas mixtures contained hydrogen with small amounts of methane. The residue consisted of the hydroxides and carbonates of sodium and potassium.

The experimental data are summarized in the following table:

Table V

I (250°); II (350°); III (350°)

Run	Glycol Used (G.)	H_2 (L.0/760) Found	H_2 (L.0/760) Theory	Per cent Theory
I	11.15	15.75	20.15	78.17
II	11.15	15.92	20.15	79.01
III	11.15	15.63	20.15	77.57

	Glycol Used (G.)	CO_2 (G.) Found	CO_2 (G.) Theory	Per cent Theory
I	11.15	13.00	15.83	82.13
II	11.15	13.66	15.83	86.30
III	11.15	13.21	15.83	83.45

	CO_2 (G.) Found	H_2 (L.0/760) Found	H_2(L.0/760) Calculated from CO_2	Per cent Calculated
I	13.00	15.75	16.55	95.17
II	13.66	15.92	17.39	91.55
III	13.21	15.63	16.82	92.93

	CH_4(L.0/760) Found
I	Trace
II	0.237
III	0.499

The data indicate that, with the exception of oxalate, traces of which were observed only in the residue from Run I, the same reaction products are formed in approximately the same quantities at both 250° and 350°, altho the velocity of the reaction is much greater at the higher temperature. The quantity of methane obtained from Run I was lower than that from Runs II and III, probably because of the solution of the gas in the water over which it was collected during the long period of 28 hours.

The experimental results from Run I verify the claim made by Nef[6] that ethylene glycol treated with excess potash-lime at 250° liberates hydrogen and forms only potassium carbonate. Nef, however, did not publish any quantitative data relating to the nature of this reaction.

Wurtz,[1] as noted, had carried out similar reactions at 250°, and had observed the formation chiefly of oxalate in the residual products. His experiments were undoubtedly carried out in a relatively short time, thus preventing the almost complete oxidation of oxalate to carbonate, which has been shown to occur very slowly at 250°.

An examination of the data in the fifth column shows that the $(CH_2OH)_2:5H_2$ ratio is lower than the $(CH_2OH)_2:2CO_2$ ratio in each case. These figures indicate that the glycol participated to some extent in a side reaction. The formation of distillate (at 350°) and the presence of methane in the gas mixtures justifies such a conclusion. The stoichiometrical ratio $2CO_2:5H_2$, however, is substantiated by the data given to the extent of 92 per cent of the theory, and warrants the assumption that at least 80 per cent of the glycol interacted with fused alkalies according to the type reaction.

G. Glycerine

The type reaction may be applied to glycerine with the following results:

$$CH_2OH.CHOH.CH_2OH + 3NaOH \longrightarrow CH_2ONa.CHONa.CH_2ONa + 3H_2O \qquad (1)$$

$$CH_2ONa.CHONa.CH_2ONa + 5HONa \longrightarrow C(ONa)_3.C(ONa)_2.C(ONa)_3 + 5H_2 \qquad (2$$

$$C(ONa)_3.C(ONa)_2.C(ONa)_3 + 4HONa \longrightarrow 3\ C(ONa)_4 + 2H_2 \qquad (3$$

$$3\ C(ONa)_4 + 3H_2O \longrightarrow 3\ Na_2CO_3 + 6NaOH \qquad (4$$

$$\sum\ 1,2,3,4.\quad CH_2OH.CHOH.CH_2OH + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \qquad (5$$

Equation 5, the summation of equations 1, 2, 3, and 4, indicates the complete oxidation of glycerine to carbonate, with the liberation of an equivalent amount of hydrogen.

In an attempt to substantiate the stoichiometrical ratios required by equation 5, experiments were conducted with glycerine and fused sodium and potassium hydroxides.

10 c.c. portions of pure, anhydrous, crystallized glycerine, supplied by the courtesy of The Globe Soap

Company, were added very slowly (about 2 drops per minute) from the Walter dropping-funnel to the equimolar mixture of fused alkalies contained in the iron tube. The temperature was kept between 345-360° for periods of 7-8 hours, and, since the gas evolution had become very slow but had not ceased after that time, the temperature was raised to 400° for 3 hours, and then to 450° for 2-3 hours. Over two-thirds of the total gas volume was collected at 350°, and the remainder was collected at the higher temperatures. After about the first four hours of heating, a slight distillate of aromatic odor appeared in quantities too small to be analyzed.

The gas mixtures contained hydrogen and small amounts of methane. The residue contained the hydroxides and carbonates of sodium and potassium.

Buisine,[7] as was noted, had reported that the reaction:

$$C_3H_5(OH)_3 + 4KOH \longrightarrow 3H_2 + CH_4 + 2K_2CO_3 + H_2O$$

occurred when glycerine and fused potassium hydroxide reacted at 320-350°, and had substantiated the ratio, $C_3H_5(OH)_3 : 4$ gas volumes, altho he had made no attempt to determine the amounts of carbonate obtained.

The presence of methane in the gas mixtures pointed to the fact that the reaction had proceeded in accordance with the equation suggested by Buisine. Calculations showed, however, that the volumes of hydrogen obtained experimentally were in excess of those required by the stoichiometrical ratio, $C_3H_5(OH)_3:3H_2$, and led to the conclusion that two simultaneous reactions had occurred: A, that obtained by the application of the type reaction, and B, that postulated by Buisine:[7]

$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 7H_2 + 3Na_2CO_3 \qquad (A)$$

$$C_3H_5(OH)_3 + 4NaOH \longrightarrow 3H_2 + CH_4 + 2Na_2CO_3 + H_2O \qquad (B)$$

The higher temperature (400-450°) used toward the end of the experiments was probably responsible for the initiation of reaction A, which Buisine had not observed at 350°.

An attempt was made to ascertain the extent to which each reaction had occurred by the calculations indicated below:

Let a = volume hydrogen obtained as result of Reaction (A)

Let b = " " " " " " " (B)

Let x = grams carbon dioxide " " " " " (A)

Let y = " " " " " " " (B)

1. Then $\frac{a}{x} = \frac{7\ H_2}{3CO_2}$

2. Then $\frac{b}{y} = \frac{3\ H_2}{2CO_2}$

3. And a + b = total volume hydrogen collected

4. And x + y = total grams carbon dioxide found in residue

The simultaneous equations 1, 2, 3, 4 were solved with the data from three runs substituted and gave the following results:

Table VI

Run	a+b(known)	x+y(known)	a (calc'd)	b (calc'd)	x (calc'd)	y (calc'd)
I	9.35 L.	10.2 g.	4.37 L.	4.98 L.	3.68 g.	6.35 g.
II	9.83 L.	11.22 g.	3.54 L.	6.30 L.	2.98 g.	8. 25 g.
III	9.21 L.	10.58 g.	3.18 L.	6.04 L.	2.68 g.	7.91 g.

Run	$C_3H_5(OH)_3$ (G. Used)	$C_3H_5(OH)_3$ (G. calc'd from x) (CO_2 Equa.A)	$C_3H_5(OH)_3$ (G. calc'd from y) (CO_2 Equa.B)	$C_3H_5(OH)_3$ Per cent calc'd. Reacting according to Equation A	$C_3H_5(OH)_3$ Per cent calc' Reacting accordi to Equation B
I	11.4	2.57	6.82	22.55	59.83
II	12.3	2.08	8.62	16.92	70.09
III	11.2	1.87	8.27	16.70	73.84

	CH_4(L.0/760) Found	CH_4(L.0/760) Calc'd from y	CH_4 Per cent theory
I	1.20	1.66	72.29
II	1.42	2.10	67.62
III	1.43	2.02	70.80

The figures indicate that about 20 per cent of the actual glycerine used reacted according to equation A, and about 70 per cent according to equation B. No claim is made that the data so calculated prove that these two reactions occur.

It is possible that the experimental results could be used equally well to substantiate other equations, but, from the point of view of the type reaction, it is logical to assume that reaction A, accounts for the excess hydrogen obtained over that required by reaction B, experimentally verified by Buisine.[7]

CONCLUSIONS

Experiments with ethyl alcohol, acetaldehyde, acetone, resorcinol, carbon monoxide, glycol, and glycerine with fused alkalies have been conducted quantitatively, by means of a special apparatus and method which provided for the bubbling of the vapors of the pure carbon compound thru an equimolar mixture of fused, dehydrated sodium and potassium hydroxides and the subsequent quantitative analysis of the resulting products.

The changes occurring during these reactions may be explained by assuming the amphoteric character of the alkali hydroxides, which enables them to dissociate as bases and as acids. Basic dissociation is shown in the formation of alcoholates, during the first steps of the reactions of the alcohols. Acidic dissociation, however, predominates and is responsible for the oxidation of the carbon compound to a stage depending on the temperature used and accompanied by the liberation of hydrogen, according to an apparently general type reaction:

$$R(H)_n + n\ HOM \qquad R(OM)_n + n\ H.H.$$

(where M = Na or K(

The equations for the interactions of ethyl alcohol, acetaldehyde, acetone, resorcinol, carbon monoxide, glycol, and glycerine, which follow a priori from the application of the type reaction mechanism and the quantitative verifications of each are summarized as follows:

Ethyl Alcohol - The incomplete reaction of ethyl alcohol at 250° and the occurrence of several simultaneous changes made it impossible to establish exact stoichiometrical ratios, but the data obtained confirmed in some measure the occurrence of the following reactions:

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CO_2Na + 2H_2$$
$$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$$
$$CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2$$
$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O$$

Acetaldehyde - Acetaldehyde reacted complete with fused alkalies at 250° to give hydrogen and acetates as the products of the reaction which conformed to the extent of 90% of the theoretical to the equation:

$$CH_3CHO + NaOH \longrightarrow CH_3CO_2Na + H_2$$

At 300° and 350°, the yields of hydrogen, methane, and carbonates were practically theoretical for the equation:

$$CH_3CHO + 2NaOH \longrightarrow H_2 + CH_4 + Na_2CO_3$$

Acetone - The reactions of acetone were analogous to those of aldehyde. At 250°, methane and acetates were the chief products of the reaction which conformed at least to the extent of 70% of the theoretical to the equation:

$$CH_3COCH_3 + NaOH \longrightarrow CH_3CO_2Na + CH_4$$

At 350°, the yields of methane and carbonates were more than 90% of the theoretical for the equation:

$$CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$$

<u>Resorcinol</u> - Resorcinol reacted with fused alkalies in an atmosphere of hydrogen at 420-490° to give a yield of hydrogen, 90.85% of the theory for all the available hydrogen in the compound, according to the type reaction:

$$C_6H_4(OH)_2 + 6NaOH \longrightarrow C(OM)_6 + 2H_2O + 4H_2$$

The evolution of hydrogen is not dependent on previous heating with access to oxygen. This reaction invalidates the claim of Boswell and Dickson[36] previously noted.

<u>Carbon monoxide</u> reacted with fused, dehydrated alkalies to the extent of about 50% at 250° to give hydrogen, carbonate and traces of formate. At 350°, carbon monoxide reacted to the extent of 75 - 85% to give hydrogen, and carbonate. The reactions occurring may be represented as follows:

$$CO + NaOH \longrightarrow HCOONa$$

$$HCOONa + NaOH \longrightarrow Na_2CO_3 + H_2$$

Glycol - Ethylene glycol reacted with fused alkalies at 250° and at 350° to give hydrogen, methane, and carbonate. The data obtained substantiate to the extent of 80% the type reaction:

$$(CH_2OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2,$$

altho the presence of methane in the gas mixtures indicates that another reaction took place to some extent.

Glycerine - Experiments with glycerine and fused alkalies at 350° - 450° indicated that two simultaneous reactions occurred:

$$(A)\quad C_3H_5(OH)_3 + 6NaOH \longrightarrow 7H_2 + 3Na_2CO_3$$

$$(B)\quad C_3H_5(OH)_3 + 4NaOH \longrightarrow 3H_2 + CH_4 + 2Na_2CO_3 + H_2O$$

The data obtained was used to show the extent to which each took place. The type reaction A occurred to the extent of 20%. Reaction B occurred to the extent of 70%.

It is interesting to note that the type reaction applied to mono-hydroxy, di-hydroxy, and tri-hydroxy alcohols gives equations that form a series:

$$CH_3OH + 2NaOH \longrightarrow 3H_2 + Na_2CO_3$$

$$(CH_2OH)_2 + 4NaOH \longrightarrow 5H_2 + 2Na_2CO_3$$

$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 7H_2 + 3Na_2CO_3$$

in which there are constant increases in the weights of hydroxide used, in the volumes of hydrogen obtained, and in the weights of carbonate obtained.

The successful application of the type reaction to mono-, di-, and tri-atomic alcohols indicates that its extension to certain of their derivatives, such as the sugars, celluloses, fats, and waxes, would be of theoretical and practical interest. As early as 1848, Löwig[21.] recorded that the interaction of cane sugar and alkalies resulted in the production of oxalate. Gottlieb[10.] studied the action of fused potassium hydroxide on cane sugar, gum, starch, and mannitol and obtained oxalates in each case. It is highly probably that such reactions, as well as those involved in the industrial preparation of oxalic acid by the oxidation of sawdust with fused alkalies, conform to the type reaction proposed. The interaction of fats and oils with caustic alkalies opens a wide field in which the application of the type reaction might prove to be of value. Reference has already been made to experiments with waxes in which the type reaction undoubtedly plays a part. The present investigation, being necessarily limited, afforded no opportunity for research on the behavior of carbohydrates, fats, or waxes with fused anhydrous alkalies, but it is to be hoped that a study of these substances from the point of view of the type reaction may be developed later.

BIBLIOGRAPHY

1. Wurtz
   - Ann. Chim. Phys. [3], 55, 417 (1859)
2. Merz and Tibirica
   - Berichte 10, 2117 (1877)
   - Berichte 13, 23 (1880)
   - J.B. 761 (1880)
3. Hell
   - Annalen 223, 269 (1884)
4. Nef
   - Annalen 318, 137 (1901)
5. Nef
   - Annalen 335, 291 & 300 (1904)
6. Nef
   - Annalen 335, 310 (1904)
7. Buisine
   - C.R. 136, 1082 (1903)
   - C.R. 136, 1204 (1903)
8. Carroll
   - J. Phys. Chem. 22, 128 (1918)
9. Peligot
   - Ann. Chim. Phys. [2], 73, 220 (1840)
10. Gottlieb
    - Annalen 52, 121 (1844)

11. Dumas and Stas
    - Annalen 35, 129 (1840)
    - Ann. Chim. Phys. [2], 73, 123 (1840)
    - Ann. Chim. Phys. [2], 73, 149 (1840)
    - C.R. 10, 260 (1840)
    - C.R. 10, 262 (1840)
12. Pelouze and Millon
    - C.R. 10, 48 (1840)
    - C.R. 10, 84 (1840)
    - Annalen 33, 182 (1840)
13. Persoz
    - C.R. 10, 326 (1840)
14. Redtenbacher
    - Annalen 47, 137 (1843)
15. Herter
    - Berichte 11, 1167 (1878)
16. Hoppe Seyler
    - Zeit. Physiol. Chemie 2, 14 (1878)
17. Belohoubek
    - Berichte 12, 1872 (1879)
    - Bl. [2], 34, 160 (1880)
18. Fernbach
    - Bl. [2], 34, 146 (1880)
19. Raisonnier
    - Bl. [3], 7, 554 (1892)

20. Lewey

Ann. Chim. Phys. [3], 13, 439 (1845)

21. Gerhardt

Ann. Chim. Phys. [3], 15, 236 (1845)

22. Löwig

"Chem. Org. Verbind", Friedrich Vieweg und
Sohn, Braunschweig, (1846)

23. Brodie

Annalen 67, 180 (1848)

Annalen 71, 149 (1848)

24. Stürcke

Annalen 223, 283 (1884)

25. Schwalb

Annalen 235, 106 (1887)

26. Berthelot

Ann. Chim. Phys. [3], 46, 477 (1856)

J.B. 216, (1858)

Ann. Chim. Phys. [3], 61, 463 (1861)

J.B. 107, (1861)

27. Erlenmeyer and Gütschow

Chem. Centralblatt 420, (1868)

28. Geuther, Frölich, and Looss

Annalen 202, 317 (1880)

29. Merz and Weith

Berichte 13, 718 (1880)

J.B. 224 (1880)

30. Haber and Bruner

Zeit. Electrochem. 10, 697 (1904)

31. Vignon

Bl. [4], 9, 18, (1911)

32. Levi and Piva

Ann. Chim. Applicata 5 , 271 (1916)

33. Gianoli

Ann. Chim. Applicata 6 , 256 (1916)

34. Bain and Tyrrell

E. J. Tyrrell Thesis - Univ. of Toronto (1917)

35. Boswell and Dickson

J.A.C.S. 40^{1}, 1773 (1918)

36. Boswell and Dickson

J.A.C.S. 47 , 2062 (1925)

37. Weitkamp

"The Amphoteric Characteristics of Sodium Hydroxide"
Thesis - University of Cincinnati (1923)

38. Feuchter

Chemiker Zeitung 38, 273 (1914)

39. Fry, Schulze, and Weitkamp

J.A.C.S. 46, 2268 (1924)

40. Fry and Schulze

E. Schulze Thesis, University of Cincinnati
(1924)

41. Fry

"The Electronic Conception of Valence and the
Constitution of Benzene"
Findlay Monograph - page 38.

42. Kurt Moers

Z. Anorg. Allgem. Chem. 113, 179 (1920)

43. Bardwell

J.A.C.S. 44, 2499 (1922)

44. Fry

Zeitsch physikal. Chem. 76, 388 (1911)

J.A.C.S. 36, 262 (1914)

"The Electronic Conception of Valence and the Constitution of Benzene" - page 22

45. Lewis

"Valence and Structure of Atoms and Molecules"

A.C.S. Monograph

page 83 (1923)

46. Fry

Zeitsch. physikal. Chem. 76, 389 (1911)

"The Electronic Conception of Valence and the Constitution of Benzene" - page 47.