In the investigations of the behavior of other monatomic alcohols and simple esters at temperatures between 450 and 550°, data have been obtained which, within the limits of experimental error necessarily entailed in the methods employed, substantiate the occurrence of the reactions predicted in conformity with the following equations originally developed by applying the type reactions, $RH_n + n\ MOH \longrightarrow R(OM)_n + n\ H_2$, and $R(CH_3)_n + n\ MOH \longrightarrow R(OM)_n + n\ CH_4$), to the molecules of the compounds investigated. In every instance oxidation of the carbon compound by the fused caustic alkalies yielded carbonates, hydrogen and methane, thus

Methyl alcohol $CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$
Ethyl alcohol $CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4$
Normal propyl alcohol $CH_3CH_2CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 5H_2 + CH_4$
*Iso*propyl alcohol $(CH_3)_2CHOH + 2NaOH \longrightarrow Na_2CO_3 + H_2 + 2CH_4$
*Iso*butyl alcohol (Extensive carbonization precluded determination of any stoichiometric ratios)
Tertiary butyl alcohol $(CH_3)_3COH + 2NaOH \longrightarrow Na_2CO_3 + 3CH_4$
Methyl formate $HCOOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2$
Methyl acetate $CH_3COOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 3H_2 + CH_4$

The following compounds resisted the action of the fused caustic alkalies: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $(CH_3)_2O$, $(C_2H_5)_2O$.

Further investigations are described in the following articles, Parts IV and V of the series.

Cincinnati, Ohio

[Contribution from the Department of Chemistry, University of Cincinnati]

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. IV. THE INTERACTION OF GLYCOL AND GLYCEROL WITH FUSED CAUSTIC ALKALIES[1]

By H. Shipley Fry and Else L. Schulze

Received August 8, 1927 Published April 5, 1928

The principles and procedure described in the preceding papers of this series[2] are here extended to a quantitative study of the interactions of the polyatomic alcohols, glycol and glycerol, with the fused eutectic mixture of sodium and potassium hydroxides.

Glycol

In 1859, Wurtz[3] found that on heating a mixture of glycol (5 g.) and potassium hydroxide (8 g.) to 250°, hydrogen (4325 cc. at 19°/768 mm.)

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[1] Summary of a section of the doctorate research of Else L. Schulze. Presented at the Philadelphia Meeting of the American Chemical Society, September, 1926.

[2] (a) Fry, Schulze and Weitkamp, This Journal, **46**, 2268 (1924); (b) Fry and Schulze, *ibid.*, **48**, 958 (1926); (c) Fry and Otto, *ibid.*, **50**, 1122 (1928).

[3] Wurtz, *Ann. chim. phys.*, [3] **55**, 417 (1859).

was evolved. The reaction residue consisted of potassium oxalate with small amounts of carbonate and glycolate. The quantities were not recorded. Wurtz proposed an equation for the reaction which, translated into modern formulas, becomes

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

The yield of hydrogen, based upon the limited quantity of alkali used, is 63% of the theoretical.

Another quantitatively significant record of the action of caustic alkalies upon glycol is that of Nef,[4] who heated equimolar quantities of ethylene glycol (60 g.) and pulverized sodium hydroxide (38.7 g.) for two and one-half hours at 230–284°. He thus obtained 25 liters of hydrogen and various products: di- and tri-ethylene glycol (17.4 g.); glycolic acid (14 g. as the calcium salt); small amounts of methyl and ethyl alcohols; and formic, acetic, oxalic and carbonic acids as sodium salts. The yields obtained do not establish stoichiometrical ratios for any particular reaction. This may be due to Nef's not having used an excess of alkali and to the manner of effecting the interaction, which did not permit the possibility of homogeneous mixing and interaction afforded by the present method.

When Nef treated ethylene glycol with an excess of potash lime at 250°, hydrogen was liberated and carbonates only were formed, but no record of the yields was noted.

An application of the proposed type reaction mechanism (that is, the type equation $R(H)_n + n\ MOH \longrightarrow R(OM)_n + n\ H_2$) to the hydrogen atoms of the glycol molecule not only serves to account for the intermediate products but also results in the development of summation equations for more complete oxidation reactions which may be verified by establishing the stoichiometrical ratios indicated therein. The scheme of partial and summation equations, involving the application of the type reaction to the hydrogen atoms united to both carbon atoms of glycol, is as follows

$$CH_2OHCH_2OH + 2NaOH \longrightarrow CH_2ONaCH_2ONa + 2H_2O \qquad (1)$$

$$CH_2ONaCH_2ONa + 4NaOH \longrightarrow C(ONa)_3C(ONa)_3 + 4H_2 \qquad (2)$$

$$C(ONa)_3C(ONa)_3 + 2H_2O \longrightarrow CO_2NaCO_2Na + 4NaOH \qquad (3)$$

$$\Sigma\ (1), (2), (3)\ CH_2OHCH_2OH + 2NaOH \longrightarrow CO_2NaCO_2Na + 4H_2 \qquad (4)$$

$$CO_2NaCO_2Na + NaOH \longrightarrow HCO_2Na + Na_2CO_3 \qquad (5)$$

$$HCO_2Na + NaOH \longrightarrow Na_2CO_3 + H_2 \qquad (6)$$

$$\Sigma\ (4), (5), (6)\ CH_2OHCH_2OH + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (7)$$

It is quite significant that equation (4), the summation of partial equations (1), (2) and (3), is identical with the reaction proposed by Wurtz. Equation (5) indicates further oxidation of the oxalate to formate and to carbonate, the products noted by Nef, while equation (7), the summation

[4] Nef, *Ann.*, **335**, 310 (1904).

of (4), (5) and (6), that is, all of the intermediate steps, represents complete oxidation of glycol to carbonate and hydrogen.

An explanation of the formation of glycolic acid, also found by Nef in the reaction residue, readily follows through the application of the type reaction mechanism when limited to the hydrogen atoms of but one of the two carbon atoms of glycol, thus

$$\begin{array}{rlr} CH_2OHCH_2OH + NaOH & \longrightarrow CH_2OHCH_2ONa + H_2O & (8) \\ CH_2OHCH_2ONa + 2NaOH & \longrightarrow CH_2OHC(ONa)_3 + 2H_2 & (9) \\ CH_2OHC(ONa)_3 + H_2O & \longrightarrow CH_2OHCO_2Na + 2NaOH & (10) \\ \Sigma\ (8),\ (9),\ (10)\ CH_2OHCH_2OH + NaOH & \longrightarrow CH_2OHCO_2Na + 2H_2 & (11) \end{array}$$

The summation of equations (8), (9) and (10) gives equation (11), which accounts for the formation of glycolic acid.

The further extension of the type reaction mechanism to the hydrogen atoms of the other carbon atom of glycolic acid gives equation (12) which, with equation (11), gives the summation equation (13) identical with summation equation (7) representing, as previously noted, complete oxidation of glycol to carbonate.

$$\begin{array}{rlr} CH_2OHCO_2Na + 3NaOH & \longrightarrow 2Na_2CO_3 + 3H_2 & (12) \\ (11),\ (12)\ CH_2OHCH_2OH + 4NaOH & \longrightarrow 2Na_2CO_3 + 5H_2 & (13) \end{array}$$

Thus the proposed reaction mechanism scheme not only explains the formation of all the intermediate and final reaction products noted by Wurtz and Nef, but also suggests the following experiments, the purpose of which is to determine how nearly the stoichiometrical ratios, $(CH_2OH)_2:CO_2:5H_2$, of summation equation (7) or (13) for complete oxidation of glycol, may be verified.

To this end runs in triplicate were conducted, one at 250° and two at 350°, with 10 cc. (11.15 g.) quantities of glycol, supplied through the courtesy of the Globe Soap Company, and purified to correct b. p. 197.5°. In each of the runs four hours was occupied in adding the glycol from the Walther dropping funnel to the fused caustic alkalies.

In the run at 250°, the evolution of hydrogen, with minute traces of methane ceased after a twenty hour heating period. No distillate was obtained. The reaction residue consisted almost entirely of the hydroxides and carbonates of sodium and potassium with small quantities of oxalates, equivalent to about 0.5 g. of oxalic acid.

In the runs at 350°, the evolution of hydrogen with traces of methane ceased after five to seven hours' heating. A distillate too minute for investigation had a characteristic aromatic odor. The reaction residue consisted entirely of the hydroxides and carbonates of sodium and potassium *with no trace of oxalates*, indicative of the complete oxidation reaction noted in equation (7) or (13).

The experimental data are summarized in Table I. All calculations are based upon summation equation (7) or (13).

TABLE I

GLYCOL DATA: RUN I (250°); RUNS II AND III (350°)

Run	$C_2H_4(OH)_2$, g.	H_2 found, liters[a]	H_2 calcd., liters[a]	H_2 calcd., %	CO_2 found, g.	CO_2 calcd., g.	CO_2 calcd., %
I	11.15	15.75	20.15	78.17	13.00	15.83	82.13
II	11.15	15.92	20.15	79.01	13.66	15.83	86.30
III	11.15	15.63	20.15	77.57	13.21	15.83	83.45

[a] At 0° and 760 mm.

The data show that the reaction for the complete oxidation of glycol at 250° and at 350° to carbonates, with the liberation of hydrogen, has been effected to the extent of practically 80% of the theoretical yields required by the proposed summation equation (7) or (13).

Glycerol

The interaction of glycerol with various alkalies has been widely investigated. A survey of the work of a number of investigators[5,4] reveals many different experimental procedures covering *wide ranges of temperatures* with *heterogeneous* reaction mixtures, and consequently a great variety of oxidation products. The few quantitative data recorded do not establish stoichiometrical relationships for any particular reactions occurring. The products obtained, *the results of partial or incomplete oxidations of glycerol by the alkalies*, are as follows: hydrogen and methane; methyl, ethyl, propyl, *iso*propyl, allyl alcohols and propylene glycol; salts of formic, acetic, lactic, acrylic, propionic, butyric, oxalic and carbonic acids.

It is the purpose of the present investigation, which employs a slow and regulated addition of glycerol, with temperature control, to a *homogeneous* reaction mixture of fused caustic alkalies: (1) to determine the possibility of verifying predictions suggested by the application of the type reaction mechanism to all of the hydrogen atoms of the glycerol molecule, thereby effecting complete oxidation of glycerol to carbonates, and (2) to consider the bearing of the *quantitative* data obtained upon the apparently contradictory observations of Buisine and of Nef.

The application of the type reaction mechanism to the glycerol molecule, resulting in a summation equation which indicates ultimate oxidation of glycerol to carbonates with the liberation of hydrogen, is as follows.

$$CH_2OHCHOHCH_2OH + 3NaOH \longrightarrow CH_2ONaCHONaCH_2ONa + 3H_2O \quad (1)$$

$$CH_2ONaCHONaCH_2ONa + 5NaOH \longrightarrow C(ONa)_3C(ONa)_2C(ONa)_3 + 5H_2 \quad (2)$$

$$C(ONa)_3C(ONa)_2C(ONa)_3 + 4NaOH \longrightarrow 3C(ONa)_4 + 2H_2 \quad (3)$$

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

$$\Sigma\ (1), (2), (3), (4) \quad CH_2OHCHOHCH_2OH + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \quad (5)$$

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[5] (a) Redtenbacher, *Ann.*, **47**, 137 (1843); (b) Herter, *Ber.*, **11**, 1167 (1878); (c) Belohoubek, *Ber.*, **12**, 1872 (1879); (d) *Bull. soc. chim.*, [2] **34**, 160 (1880); (e) Fernbach, *ibid.*, [2] **34**, 146 (1880); (f) Raisonnier, *ibid.*, [3] **7**, 534 (1892); (g) Buisine, *Compt. rend.*, **136**, 1082, 1204 (1903).

The extent to which the summation equation (5) may be verified will be considered after reviewing briefly the pertinent work of Buisine and of Nef.

Buisine[5a] studied the reactions of glycerol at various temperatures with *an excess of potassium hydroxide mixed with potash lime* in order to establish a method for the quantitative determination of small amounts of glycerol calculated upon the volume of hydrogen liberated. The temperatures and the equations for the corresponding reactions postulated by Buisine are as follows:

$$\text{220–250°}\quad C_3H_8O_3 + 2KOH \longrightarrow CH_3CO_2K + HCO_2K + H_2O + 2H_2 \qquad (6)$$

$$\text{250–280°}\quad 2C_3H_8O_3 + 4KOH \longrightarrow 2CH_3CO_2K + K_2C_2O_4 + 2H_2O + 5H_2 \qquad (7)$$

$$\text{280–320°}\quad 2C_3H_8O_3 + 6KOH \longrightarrow 2CH_3CO_2K + 2K_2CO_3 + 2H_2O + 6H_2 \qquad (8)$$

$$\text{320–350°}\quad C_3H_8O_3 + 4KOH \longrightarrow 2K_2CO_3 + CH_4 + H_2O + 3H_2 \qquad (9)$$

Buisine recommended the employment of equations (8) and (9) at 320 and 350°, respectively, as best adapted to give yields of hydrogen for calculating quantities of glycerol, but he recorded no quantitative data other than the volumes of gases evolved to verify the other stoichiometrical requirements for the yields of the other intermediate oxidation products, namely, the formates, acetates, oxalates and carbonates of potassium. Nevertheless, it is quite significant that equations (6), (7), (8) and (9) represent successive and further degrees of oxidation of glycerol occurring as the temperature increases. The ultimate oxidation to carbonate only (see Equation 5 in preceding reaction mechanism scheme) was not considered by Buisine. It should also be noted that each of Buisine's equations may be derived, *a priori*, by an application of the type reaction mechanism to a selected number of the hydrogen atoms of the glycerol molecule, but when all are involved, presumably at higher temperature, the reaction represented by equation (5) occurs, as will be shown later.

Nef heated 309 g. of glycerol and 137 g. of pulverized sodium hydroxide at 270–280° from six to eight hours and obtained methyl, propyl and allyl alcohols, lactic and propionic acids and salts of oxalic and carbonic acids. No record was noted of the quantity of hydrogen liberated in this experiment. *The quantity of alkali used by Nef was considerably less than that required for the completion of any of the reactions postulated by Buisine.* In another experiment Nef heated, at 270–325° for three hours, 20 g. of glycerol with 60 g. of potash lime, *not an excess* as employed by Buisine but comparable to the quantity required by the Buisine equation (8), and obtained predominantly the salts of propionic and carbonic acids with traces of formates, oxalates and acetates, and twelve liters of hydrogen. Buisine, *at the same temperature (280–320°), but with an excess of potash lime, obtained only acetates and carbonates and a practically theoretical yield of hydrogen (Equation 8).* The corresponding yield of hydrogen obtained by Nef without an excess of potash lime was about 40% of the theoretical.

These marked differences in the results of Buisine and Nef find an explanation in the fact that Buisine employed an excess of alkali while Nef did not. Furthermore, the number of intermediate reaction products, indicative of limited oxidation of glycerol, is decreased as the temperature is increased. At sufficiently high temperature oxidation primarily to carbonates is effected. These conclusions are further substantiated by the quantitative data obtained in the following runs with glycerol.

Three runs were conducted, each with approximately 10 cc. of previously crystallized glycerol (b. p. 290°), supplied through the courtesy of the Globe Soap Company, and added at the rate of two drops per minute to the excess of the fused caustic alkalies. The temperature was maintained at 345–360° for eight hours, at the end of which time gas evolution had almost ceased. The temperature was then raised to and maintained at 400° for three hours, thereby effecting the evolution of more gas, which finally ceased after heating at 450° for another three hours. About two-thirds of the total volume of gases evolved was collected at 350°. *The apparent cessation of the reactions at 350° indicated completion of the intermediate oxidation reactions noted in the Buisine equations (6), (7), (8) and (9), while further heating at 400° and at 450° promoted the reaction of the previously developed equation (5) representing oxidation solely to carbonate.*

Since it has been found in the three runs made that *the reaction residue contained only carbonates* and that *the gases evolved were hydrogen and methane in the volume ratio of about* $5H_2:CH_4$, the conclusion is apparent that *two reactions* were ultimately concurrent, namely, that of the Buisine equation (9) yielding hydrogen, methane and carbonates in the stoichiometrical ratio $3H_2:CH_4:2CO_2$ and that of equation (5) yielding hydrogen and carbonates in the stoichiometrical ratio $7H_2:3CO_2$.

In order to facilitate record and subsequent reference, the complete oxidation equation (5) will now be designated as reaction (A) and the Buisine equation (9) for partial oxidation as reaction (B), thus

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

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

and the quantitative data of the three runs may be employed to calculate approximately the extent to which reactions (A) and (B) occurred.

If a and b represent the respective volumes of hydrogen liberated, and x and y the respective yields of carbonates (as CO_2) in the reactions (A) and (B), then $a:x = 7H_2:3CO_2$ and $b:y = 3H_2:2CO_2$. Having determined $(a + b)$ and $(x + y)$, the quantities of glycerol respectively oxidized by the caustic alkalies according to reactions (A) and (B) may be calculated. The analytical data and results of these calculations are summarized in Table II.

The analytical data and calculations indicate that within the limits of experimental error necessarily involved in the methods of procedure, an average of 18.72% of the initial quantity of glycerol employed was completely oxidized to carbonate according to reaction (A), while an average of 67.92% was partially oxidized to carbonate according to re-

TABLE II

GLYCEROL DATA

Run	H = $(a + b)$, liters[a]	$CO_2 = (x + y)$, g.	(a) liters[a] calcd.	(b) liters[a] calcd.	(x), g., calcd.	(y), g., calcd.
I	9.35	10.2	4.37	4.98	3.68	6.35
II	9.83	11.22	3.54	6.30	2.98	8.25
III	9.21	10.58	3.18	6.04	2.68	7.91
Average	9.46	10.67	3.70	5.77	3.11	7.50

Run	$C_3H_5(OH)_3$, g. used	$C_3H_5(OH)_3$, g. $\Leftrightarrow x$ eq. (A)	$C_3H_5(OH)_3$, g. $\Leftrightarrow y$ eq. (B)	$C_3H_5(OH)_3$, % reacting, eq. (A)	$C_3H_5(OH)_3$, % reacting, eq. (B)
I	11.4	2.57	6.82	22.55	59.85
II	12.3	2.08	8.62	16.92	70.09
III	11.2	1.87	8.27	16.70	73.84
Average	11.6	2.17	7.90	18.72	67.92

[a] At 0° and 760 mm.

action (B). Thus 86.64% average of all of the glycerol used may be accounted for in terms of reactions (A) and (B), the former dominating at about 450°, while the latter, according to Buisine, is the dominant reaction at 350°. If the quantity of glycerol escaping interaction (about 14% of the initial quantity used amounting to 1.6 g., which represents the amount very likely adhering to the walls of the apparatus) be disregarded, then of the glycerol entering into reaction 21% was oxidized according to reaction (A) and 78% according to reaction (B).

Summary

The application of the type reaction mechanism to the glycol and glycerol molecules leads to the development of equations for reactions accounting for the intermediate and final products obtained by previous investigators.

The apparently contradictory results of Buisine and of Nef have been explained by showing that the various oxidation products obtained are dependent upon the quantities of alkalies used, the temperatures employed, time of heating and the homogeneity of the reaction mixtures. As the temperature is increased, fused alkalies being present in large excess, further oxidation occurs and fewer intermediate products are obtained; at sufficiently high temperatures complete oxidation to carbonates with the liberation of hydrogen is effected.

Under the special method of investigating the oxidizing action of the fused sodium and potassium hydroxides upon glycol and glycerol, which permits *their slow addition to a homogeneous reaction mixture with constant temperature control,* quantitative data have been obtained which indicate the occurrence of the following reactions: complete oxidation of glycol at 350° to carbonates with liberation of hydrogen (Equation 5); partial oxidation of glycerol at 350° to carbonates with the liberation of hydrogen and methane (Reaction B), while complete oxidation to carbonates with

the liberation of hydrogen (Reaction A) is promoted by raising the temperature to 450°. At 450° about 20% of the glycerol was oxidized according to reaction (A) and 78% according to reaction (B).

The proposed equations for these reactions, derived through an application of the type reaction mechanism and quantitatively verified within the limits of experimental error necessarily entailed in the method of procedure, are as follows

$$C_2H_4(OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \quad (5)$$
$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \quad (A)$$
$$C_3H_5(OH)_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 3H_2 + CH_4 + H_2O \quad (B)$$

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. V. THE INTERACTION OF DEXTROSE, LEVULOSE, SUCROSE AND CELLULOSE WITH FUSED CAUSTIC ALKALIES[1]

BY H. SHIPLEY FRY AND EARL OTTO

RECEIVED AUGUST 8, 1927 PUBLISHED APRIL 5, 1928

Introduction

The results obtained in a quantitative study of the interaction of a number of monatomic alcohols[2] and the polyatomic alcohols, glycol and glycerol,[3] with a eutectic mixture of fused sodium and potassium hydroxides naturally leads to an extension of the previously described principles and procedure[4] to several polyhydroxy compounds—dextrose, levulose, sucrose and cellulose.

The type reaction mechanism applied to sugars and cellulose leads to equations accounting for a great variety of intermediately formed oxidation products; but since, in this study, the carbon compounds have been either (1) completely oxidized to carbonate with the liberation of hydrogen or (2) partially oxidized to carbonate with the liberation of methane and hydrogen, only these two types of reactions will be considered.

Dextrose and Levulose

The literature records no quantitatively verified equations for such specific reactions of dextrose and levulose with the caustic alkalies under

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[1] Synopsis of a section of a thesis presented by Earl Otto to the Faculty of the Graduate School, University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Read before the Lexington Section, February 9, 1927, and the Cincinnati Section, February 23, 1927, of the American Chemical Society.

[2] Fry and Otto, THIS JOURNAL, **50,** 1122 (1928).

[3] Fry and Schulze, *ibid.*, **50,** 1131 (1928).

[4] (a) Fry, Schulze and Weitkamp, *ibid.*, **46,** 2268 (1924); (b) Fry and Schulze, *ibid.*, **48,** 958 (1926); see also (c) Fry and Cameron, *ibid.*, **49,** 864 (1927).