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

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS[1]

I. THE INTERACTION OF ACETYLENE, METHYL ALCOHOL AND FORMALDEHYDE WITH FUSED CAUSTIC ALKALIES

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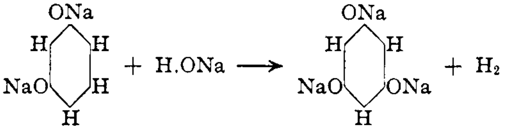
Introduction

Comparatively few reactions are recorded in which hydrogen may be liberated directly from carbon compounds and references to the quantitative study of such reactions are rare. Wurtz, in a study of the oxidation of diatomic alcohols[3] found that glycol on fusion with potassium hydroxide yielded chiefly hydrogen and potassium oxalate, presumably according to the equation, $C_2H_6O_2 + 2KOH \longrightarrow K_2C_2O_4 + 4H_2$. The yield of hydrogen was about 58% of that required by the reaction. (A quantitative study of this reaction is contemplated.)

Another reaction, one of marked theoretical and practical importance, is met in the conversion of resorcinol into phloroglucinol on fusion with sodium hydroxide. A vigorous evolution of hydrogen occurs, the cessation of which marks the end of the change,



These reactions indicate the amphoteric character of sodium hydroxide which more commonly (in aqueous media) undergoes basic dissociation, $NaOH \longrightarrow Na^+ + OH^-$, but here (in the fused state) acts *both as an acid and an oxidizing agent*,[4] $HONa \longrightarrow H^+ + ONa^-$.

Another reaction involving the acid dissociation and oxidizing action of sodium hydroxide with the concomitant liberation of hydrogen, reported by Feuchter,[5] occurs when dry acetylene is passed through an equimolecular mixture of sodium and potassium hydroxides in a nickel vessel at 220°. A 60% yield of alkali ortho-acetates was obtained.

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[1] Read before the Cincinnati Section of the American Chemical Society, November 14, 1923, and before Section C (Chemistry), American Association for the Advancement of Science, December 29, 1923.

[2] This article is based upon the theses presented to the Faculty of the Graduate School, University of Cincinnati, by Helen Weitkamp and Else L. Schulze in partial fulfilment of the requirements for the degree of Master of Arts.

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

[4] The substitution of negative oxysodium radicals in *meta* positions to each other in resorcinol and phloroglucinol completely conforms with the polar valence formula of benzene proposed by Fry, "The Electronic Conception of Valence and the Constitution of Benzene," Longmans, Green and Co., **1921.**

[5] Feuchter, *Chem.-Ztg.*, **38,** 273 (1914).

Feuchter explains this oxidation of acetylene to acetic acid as being dependent upon, first, the addition of two molecules of sodium hydroxide to one of acetylene,

$$HC{\equiv}CH + 2HONa \longrightarrow CH_3{-}C(ONa)_2H \qquad (1)$$

and, second, the interaction of the addition compound with another molecule of sodium hydroxide yielding sodium ortho-acetate and hydrogen,

$$CH_3{-}C(ONa)_2H + HONa \longrightarrow CH_3{-}C(ONa)_3 + H_2 \qquad (2)$$

Reaction 1 is perfectly analogous to the addition of two molecules of hydrogen halide (H^+X^-) to acetylene, while (2) is exactly parallel to the previously noted interaction between glycol and potassium hydroxide and between resorcinol and sodium hydroxide. These facts lead to the assumption that we are dealing with examples of a general reaction of the type, $R(H)_n + n\text{HONa} \longrightarrow R(ONa)_n + nH_2$, in which R is a more or less complex radical containing carbon.

A prototype of this general reaction may be found in the hydrolyses of metal hydrides which one of us[6] assumed to embody negatively functioning hydrogen atoms and predicted that such hydrides on electrolysis would yield the metal at the cathode and hydrogen at the anode. This prediction was first verified by Kurt Moers[7] who obtained hydrogen at the anode during the electrolysis of lithium hydride. Subsequently D. C. Bardwell[8] experimenting with calcium hydride, and Kurt Peters[9] repeating the work of Moers with lithium hydride, obtained hydrogen at the anode in amounts corresponding accurately to Faraday's law.

Accordingly, the hydrolysis of lithium hydride on the one hand and the interaction of a carbon compound on the other may be represented in terms of polar formulas as parallel reactions.

$$Li^+.H^- + H^+.OH^- \longrightarrow Li^+.OH^- + H^+.H^-$$
$$R^+.H^- + H^+.ONa^- \longrightarrow R^+.ONa^- + H^+.H^-.$$

In other words, certain compounds and special conditions indicate that hydrogen atoms, either in inorganic or in carbon compounds, may function negatively. G. N. Lewis[10] states that "even a symmetrical molecule like that of H_2 or I_2 may from time to time become polarized in one direction or the other, as a consequence of the disturbance due to thermal motion."

In a quantitative study of some new reactions herewith to be described, evidence is adduced to show that as a likely consequence of disturbance due to thermal conditions, negative radicals of the formula OM^- ($M =$ Na or K) displace negative hydrogen atoms (H^-) attached to carbon, thereby effecting an oxidation of the carbon compounds with the liberation

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[6] Fry, This Journal, **36,** 268 (1914).

[7] Moers, *Z. anorg. allgem. Chem.*, **113,** 179 (1920).

[8] Bardwell, This Journal, **44,** 2499 (1922).

[9] Peters, *Z. anorg. allgem. Chem.*, **131,** 140 (1923).

[10] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923,** p. 83.

of molecular hydrogen. The compounds considered in this paper are acetylene, methyl alcohol and formaldehyde.

Apparatus

The apparatus in which these reactions were conducted was designed so that the *vapors* of the carbon compounds under investigation would bubble through an equimolar gram mixture of fused sodium and potassium hydroxides. It consisted of an outer iron tube, 30 cm. long by 5 cm. in diameter, threaded at both ends, closed at its lower end with a cap and charged with an equimolar mixture of hydroxides, previously fused at red heat to insure complete absence of water. The lower closed end of the outer tube was submerged to a depth of 9 cm. in a bath of molten solder. The temperature of the bath was regulated with a Meker burner, a Brown pyrometer furnishing temperature readings.

The upper end of the outer iron tube was closed by a reducing coupling through which passed, securely screwed thereto, an inner iron tube 40 cm. in length and 2.5 cm. in diameter. The lower dentated end of this inner tube extended to within 0.5 cm. of the bottom of the outer tube and was thus submerged to a depth of 6 cm. in the fused alkali mixture. An iron exit tube 20 cm. long and 1 cm. in diameter was screwed at right angles into the top of the outer iron tube, at a point 3 cm. below the reducing coupling, and inclined slightly to the base of the outer tube. In short, the apparatus described functioned as a simple gas-washing bottle.

The carbon compounds were volatilized and their vapors passed through the inner iron tube directly into and through the fused alkalies. Any volatile products formed escaped through the exit tube which was attached to a Liebig condenser. The receiver at the lower end of the condenser was a gas-washing bottle, submerged in a freezing mixture, which retained any liquefiable products. Finally, a tube from the receiver conveyed any evolved gases to a pneumatic trough for collection over water in bottles of graduated capacity.

Experimental Part

A. Acetylene

To test the apparatus and method of operation, Feuchter's reaction of acetylene with fused alkalies was reinvestigated. Only a synopsis of the results of many experiments is noted here.

Acetylene,[11] prepared from calcium carbide, was led from a graduated gasometer through a calcium chloride drying tower and thence through the inner iron tube of the apparatus which bore a charge of equimolar weights

[11] Since the acetylene was used directly without special purification, it is likely that by-products, naturally formed in its preparation, would vitiate exact quantitative determination of the gases involved by the action of the fused alkalies. Consequently, the data with respect to acetylene are regarded as only approximately quantitative.

of fused sodium and potassium hydroxides (Kahlbaum) maintained at a temperature of 300–325°. Acetylene was passed into the alkalies at the approximate rate of 4 liters per hour. No volatile products were collected in the receiver but various volumes of gases were evolved, collected and subsequently analyzed.

Feuchter[5] stated that for every volume of acetylene introduced, one-half volume of hydrogen was obtained and the fused alkalies were converted into acetates (60% yield). In numerous experiments we found that the volume of acetylene that reacted with the fused alkalies, before they became too viscous to permit further action and passage of the gases, yielded from one to ten gas volumes. Consecutive samples of the gases evolved during the various runs were found on analysis to contain various quantities of hydrogen and methane ranging in proportion by volume from 8:1 to 1:1. They were also accompanied by minute traces of unsaturated hydrocarbons.

By repeated analyses the reaction residues from the fused alkalies were found to contain *no acetates but various quantities of carbonates* (alkalimeter determinations). The presence of carbonates shows that in addition to Reactions 1 and 2 proposed by Feuchter, a third consecutive reaction (3), the well-known conversion of acetate to carbonate with the liberation of methane, takes place.

$$HC{\equiv}CH + 2HONa \longrightarrow CH_3{-}C(ONa)_2H \tag{1}$$

$$CH_3{-}C(ONa)_2H + HONa \longrightarrow CH_3{-}C(ONa)_3 + H_2 \tag{2}$$

$$CH_3{-}C(ONa)_3 + HONa \longrightarrow CH_4 + C(ONa)_4 \tag{3}$$

The summation of (1), (2) and (3) gives Equation 4.

$$C_2H_2 + 4NaOH \longrightarrow H_2 + CH_4 + C(ONa)_4 \tag{4}$$

The percentage yields of carbon dioxide in the reaction residue (sodium and potassium orthocarbonates) were only roughly proportioned to the quantities of acetylene introduced into the fused alkalies. Repeated experiments and analyses failed to establish any stoichiometrical relationships (based upon Equation 4) either between the amounts of acetylene and carbonate, or between the carbonate and the volumes of hydrogen and methane evolved.

The reaction residues invariably contained free carbon which indicates other decompositions of acetylene. The simple concurrent decomposition, $C_2H_2 \longrightarrow 2C + H_2$, would not only account for the excessive yield of hydrogen over methane, but also explain the impossibility of checking the quantitative yields of hydrogen, methane and carbonate in terms of Equation 4. A further study of the interaction of acetylene with fused caustic alkalies is proposed, since the present work shows that under the conditions described acetylene may be oxidized to the carbonic acid stage accompanied by the liberation of hydrogen and methane.

Experiments similar to those described above were conducted with ethylene. No evidence was obtained to indicate that it reacts with fused caustic alkalies.

More direct confirmation of the acidic dissociation of fused sodium and potassium hydroxides and their oxidizing action, accompanied by the liberation of hydrogen, is found in the following quantitative study of the reactions with (B) methyl alcohol and (C) formaldehyde.

B. Methyl Alcohol

The general type reaction, $R(H)_n + n\text{HONa} \longrightarrow R(\text{ONa})_n + nH_2$, suggests some interesting possibilities when applied to methyl alcohol. They are indicated and summarized as follows.

$$CH_3OH + NaOH \longrightarrow CH_3ONa + H_2O \tag{3}$$
$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \tag{4}$$
$$CH_3(ONa)_2 + H_2O \longrightarrow CH_2O + 2HONa \tag{5}$$

$$\text{I}, \Sigma\ (3), (4), (5), CH_3OH \longrightarrow CH_2O + H_2$$

$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \tag{6}$$
$$CH(ONa)_3 + H_2O \longrightarrow HCO_2Na + 2NaOH \tag{7}$$

$$\text{II}, \Sigma\ (3), (4), (6), (7), CH_3OH + HONa \longrightarrow HCO_2Na + 2H_2$$

$$CH(ONa)_3 + HONa \longrightarrow C(ONa)_4 + H_2 \tag{8}$$
$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \tag{9}$$

$$\text{III}, \Sigma\ (3), (4), (6), (8), (9), CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$$

The summations of consecutive Type Reactions 3, 4 and 5, 3, 4, 6 and 7, and 3, 4, 6, 8 and 9 give, respectively, three equations, I, II and III, which are significant in that they indicate possible mechanisms of reactions involved in oxidizing methyl alcohol successively to the formaldehyde, formic acid and carbonic acid stages. If Equation III is consummated then Reactions 3, 4, 6, 8 and 9 may be regarded as consecutive and the type reaction, $R(H)_n + n\text{HONa} \longrightarrow R(\text{ONa})_n + nH_2$, is validated. The following quantitative experiments with methyl alcohol have been performed to this end.

Methyl alcohol vapor was brought into interaction with an equimolar mixture of fused sodium and potassium hydroxides by attaching a Walter dropping funnel, containing 10 cc. of methyl 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 through 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 slow steady current of the alcohol vapor to pass through the fused alkalies which were maintained at a temperature of 300–325°.

In each of the three following runs, only 10 cc. of methyl alcohol was vaporized and passed into an excess of the fused alkalies at such a rate that decomposition of the alcohol was complete. No methyl alcohol was detected in the condenser or receiver. The duration of each run was about three hours and 15 liters of gas (under standard conditions) was collected and analyzed. Ten successive samples from the first run, four from the second and thirteen from the third were separately exploded with an excess of oxygen. The volumes of residual oxygen show that the gas evolved was pure hydrogen. The gas analyses of each run are summarized as follows.

Table I

Run	H_2 samples Cc. collectively	Total O_2 Cc.	Residual O_2 Cc. found	Residual O_2 Cc. calc.
I	104.15	215.30	165.23	163.23
II	38.30	86.50	67.60	67.35
III	146.00	272.86	202.17	199.86

Evidence that the fused alkalies, when acted upon by an excess of methyl alcohol, are transformed quantitatively to carbonates is afforded by a run in which methyl alcohol vapor was passed through the fusion mixture until hydrogen was no longer evolved and the excess of methyl alcohol added was condensed and recovered in the receiver; 0.5g. samples of the white reaction residue from the iron tube proved to be an equimolecular mixture of sodium and potassium carbonate, since on conversion to sulfate, by the customary quantitative procedure, there was obtained 0.6505 g. or 100.4% of the calculated quantity (0.6479 g.) of the corresponding sulfates.

Other runs were made to determine the ratios of the amount of methyl alcohol interacting (fused alkalies being in excess), to the amount of carbonates formed (determined as carbon dioxide) and to the volumes of hydrogen evolved. According to the equation for the reaction, $CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$, these ratios are, respectively, $CH_3OH:CO_2$ and $CH_3OH:3H_2$. The total amounts of carbonates formed were found by alkalimeter determinations of the carbon dioxide content of aliquot portions of the reaction mixture. The volumes of hydrogen evolved are noted at standard conditions.

Table II

CH_3OH G.	CO_2 Found G.	CO_2 Calcd. G.	% Calcd.
7.8673	10.31	10.82	95.29
7.8673	10.57	10.82	97.69
7.7792	10.54	10.70	98.50
	H_2 (1. 0/760) Found	H_2 (1. 0/760) Calcd.	
7.8673	14.06	16.53	85.06
7.8673	14.04	16.53	84.94
7.7792	15.60	16.34	95.40

The data in Table II indicate that the quantities of carbon dioxide and hydrogen obtained confirm (within the limits of experimental error unavoidably due to the type of apparatus, conditions and manipulations involved) the ratios, $CH_3OH:CO_2:3H_2$, required by the equation for the reaction between methyl alcohol and fused caustic alkalies.

Further confirmation of the type reaction is afforded in the following experiments with trioxymethylene (formaldehyde).

C. Formaldehyde

According to the mechanism of the general type reactions proposed in part B, the reaction between formaldehyde and fused caustic alkalies should conform to the equation, $OCH_2 + 2HONa \longrightarrow OC(ONa)_2 + 2H_2$, which requires the establishment of the stoichiometrical ratio, $CO_2:2H_2$.

The interaction of formaldehyde as a gas with an equimolar mixture of fused sodium and potassium hydroxides (300–325°) was effected by placing a weighed quantity of trioxymethylene in a 100cc. short-neck, round-bottom flask connected by a short glass tube (8 mm. in diameter) to the upper end of the inner tube of the apparatus. The entire flask was submerged in a glycerol bath, gently heated to and maintained throughout the course of the reaction at 150°. Thus the trioxymethylene was depolymerized to formaldehyde, $(CH_2O)_3 \longrightarrow 3CH_2O$, which passed slowly and steadily into the fused alkalies. The first three runs were conducted for the purpose of establishing the nature of the gas which was copiously evolved (10 g. of formaldehyde usually gave about 13 liters of gas); it was collected over water, and on subsequent explosions with an excess of oxygen proved to be hydrogen. Seven successive samples from the first run, five from the second and fourteen from the third were separately exploded. Collectively tabulated, the results are given in Table III.

Table III

Run	H_2 samples Cc. collectively	Total O_2 Cc.	Residual O_2 Cc. found	Residual O_2 Cc. calcd.
I	78.83	142.85	104.50	103.44
II	64.95	101.55	69.75	69.08
III	137.55	312.95	248.32	244.17

Other runs were made to determine the ratios of the amounts of formaldehyde reacting with an excess of fused alkalies to the quantities of carbonates found (by carbon dioxide determinations in aliquot portions of the reaction mixture) and to the volumes of hydrogen evolved (calculated

Table IV

CH_2O G.	CO_2 Found G.	CO_2 Calcd. G.	% Calcd.
14.82	19.17	21.76	88.09
11.90	15.57	17.46	89.18
	H_2 (l. 0/760) Found	H_2 (l. 0/760) Calcd.	
14.82	19.93	22.14	90.02
11.90	16.07	17.77	90.44

to standard conditions). According to the proposed reaction, the ratios are $CH_2O:CO_2$ and $CH_2O:2H_2$. The difference between the weight of the 100cc. flask (originally containing 10 to 20 g. of trioxymethylene) with connections thereto, before heating, and its weight after heating, gave the weight of formaldehyde reacting with the alkalies.

The experimental data show that the actual quantities of carbonate formed and hydrogen evolved are practically 90% of those required by calculation. These yields would have been nearer the calculated had it been possible to effect complete reaction of the formaldehyde (from the depolymerization of the trioxymethylene) with the fused alkalies. This was prevented by a partial repolymerization of formaldehyde to trioxymethylene which invariably took place on the upper inner surface of the central iron tube of the apparatus and thereby escaped interaction. Nevertheless, it is quite significant that the amounts of formaldehyde that did react gave almost identical percentages of the calculated yields of carbon dioxide and hydrogen which are in the ratio $CO_2:2H_2$ and thus validate the reaction, $CH_2O + 2NaOH \longrightarrow Na_2CO_3 + 2H_2$.

It is a pleasure to acknowledge the gift of fellowship stipends by Dr. Ernst Twitchell which makes possible further study of some of these reactions by Miss Else L. Schulze.

Summary

Experiments conducted on a quantitative basis show that certain compounds in the vapor state interact with fused caustic alkalies according to an apparently general type reaction (M = Na or K): $R(H)_n + n\text{MOH} \longrightarrow R(OM)_n + nH_2$. This reaction involves the acidic dissociation of the alkalies, oxidation of the carbon compounds to carbonates through the replacement of hydrogen atoms by OM^- radicals, and the liberation of hydrogen.

(a) Acetylene, (b) methyl alcohol and (c) formaldehyde are, respectively, oxidized to the orthocarbonate or carbonate stage according to the following reactions,

$$C_2H_2 + 4MOH \longrightarrow M_4CO_4 + H_2 + CH_4 \tag{a}$$
$$CH_3OH + 2MOH \longrightarrow M_2CO_3 + 3H_2 \tag{b}$$
$$CH_2O + 2MOH \longrightarrow M_2CO_3 + 2H_2 \tag{c}$$

Quantitative data indicate that the amounts of hydrogen evolved and of carbonates formed in Reactions (b) and (c) closely approximate, respectively, the theoretical ratios $3H_2:CO_2$ and $2H_2:CO_2$.

This research will continue, from the point of view of the apparently general type reaction, with further investigations of the interaction with fused alkalies not only of hydrocarbons, alcohols, aldehydes and acids but also of alkyl halides, esters and other derivatives of organic acids. The oxidation of cellulose by fused alkalies to yield oxalates undoubtedly conforms to the type reaction proposed.

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