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

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. III. THE INTERACTION OF MONATOMIC ALCOHOLS AND ESTERS WITH FUSED CAUSTIC ALKALIES[1]

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Introduction

Previous papers[2] have described the apparatus, experiments, and analytical methods employed, and the hypothesis proposed for the mechanism of the reactions occurring when the vapors of methyl alcohol, ethyl alcohol, formaldehyde, acetaldehyde and acetone were bubbled through an excess of fused, anhydrous equimolar mixtures of sodium and potassium hydroxides.

The *quantitative* investigations of these reactions showed that the carbon compounds undergo oxidation, usually to carbonates, with the liberation of hydrogen and frequently methane, in conformity with the general type reactions (M = Na or K)

$$R(H)_n + n\,MOH \longrightarrow R(OM)_n + n\,H_2$$
$$R(CH_3)_n + n\,MOH \longrightarrow R(OM)_n + n\,CH_4$$

These reactions apparently involve the acidic dissociation of the alkalies and the replacement of hydrogen or methyl radicals by OM radicals.

The present paper presents the results of an extension of the previously described procedure and principles to a further study of the reactions of (A) methyl and (B) ethyl alcohols and to an initial study of other monatomic alcohols—(C) normal propyl, (D) secondary propyl, (E) *iso*butyl and (F) tertiary butyl alcohols—and the simple esters, (G) methyl formate and (H) methyl acetate.

A. Methyl Alcohol

This further study of the behavior of methyl alcohol was suggested by a comment of one of the editors of THIS JOURNAL, to the effect that in order to make the argument more rigid, more attention should have been given to the intermediate steps involved in the proposed reaction mechanism scheme. These steps were assumed, in the case of methyl alcohol, to conform to the following scheme of consecutive reactions

$$CH_3OH + NaOH \longrightarrow CH_3ONa + H_2O \qquad (1)$$
$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (2)$$

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[1] Synopsis of a section of a thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Earl Otto, in partial fulfilment of the requirements for the degree of Doctor of Philosophy; also presented in part 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 Cameron, *ibid.*, **49**, 864 (1927).

$$CH_2(ONa)_2 + H_2O \longrightarrow CH_2O + 2HONa \tag{3}$$

$$\text{I, } \Sigma\ (1), (2), (3), CH_3OH \longrightarrow CH_2O + H_2$$

$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \tag{4}$$

$$CH(ONa)_3 + H_2O \longrightarrow HCO_2Na + 2NaOH \tag{5}$$

$$\text{II, } \Sigma\ (1), (2), (4), (5), CH_3OH + HONa \longrightarrow HCO_2Na + 2H_2$$

$$CH(ONa)_3 + HONa \longrightarrow C(ONa)_4 + H_2 \tag{6}$$

$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \tag{7}$$

$$\text{III, } \Sigma\ (1), (2), (4), (6), (7), CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$$

As evidence for this scheme, the summation reaction noted in Equation III and also the conversion of formaldehyde to carbonate with the liberation of hydrogen in conformity with the type equation, $CH_2O + 2NaOH \longrightarrow Na_2CO_3 + 2H_2$, have been quantitatively verified. Each of these reactions was effected at 300–325°, at which temperatures the intermediately formed methylate, formaldehyde and formic acid compounds of the alkali metals, indicated in partial Equations 1, 2 and 4, are quite unstable. They undoubtedly, as noted shortly, undergo immediate and practically complete oxidation at 300° to the final carbonate stage culminating in summation Equation III.

In order to secure further evidence for the occurrence of intermediate reactions, it was deemed advisable to conduct a series of eight independent runs, each in duplicate, with methyl alcohol, extending over a range of temperatures from 250 to 450°, and estimating quantitatively for each run the yields of hydrogen, carbonates and methyl alcohol present as methylates, and testing further the reaction residues for the presence of formaldehyde and formates predicted at lower temperatures.

In each run 10 cc. or 7.89 g. of absolute methyl alcohol was used. In place of the formerly employed equimolar mixture of the caustic alkalies, a eutectic mixture, melting point 185°, was used, namely, 51.1 g. of potassium hydroxide with 55.3 g. of sodium hydroxide. The yields of hydrogen and carbonates were determined as described in previous papers. The amounts of unaffected methyl alcohol present in the reaction residues as methylates of sodium and potassium were determined by alkaline permanganate titrations upon aliquot portions.

Formaldehyde was not found in any of the reaction residues. This was to be expected, since a separate run made at 250° with formaldehyde (obtained through depolymerization of trioxymethylene) showed practically complete oxidation to carbonate with only minute traces of intermediately formed alkali formates. In fact, the quantities of formates actually obtained (determined by the extent of their reducing action upon mercuric chloride), in the first four runs, namely at 250, 270, 290 and 310°, ranged from about 0.2 to 0.0%.

In Table I, following, the data for each temperature indicate the extent of the oxidation of methyl alcohol according to Equation III. Each figure is an average of two runs which checked within 5%.

TABLE I

THE EFFECT OF TEMPERATURE UPON THE INTERACTION OF METHYL ALCOHOL WITH FUSED CAUSTIC ALKALIES

Run	Temp., °C.	H_2 found, liters (0°/760 mm.)	H_2 calcd., % (eq. III)	CO_2 found, g.	CO_2 calcd., % (eq. III)	CH_3OH, g. recovered	CH_3OH, % recovered
1	250	0.9	5.6	0.73	6.7	7.19	91.1
2	270	2.6	16.0	2.02	18.8	5.65	71.6
3	290	7.6	46.1	5.24	48.6	2.09	26.6
4	310	12.8	76.9	7.68	71.2	.75	9.6
5	330	14.0	86.0	8.79	81.4	.19	2.4
6	350	14.4	86.9	8.92	82.6	.15	1.9
7	370	14.5	87.4	9.20	85.2	.09	1.3
8	450	16.6	99.9	10.69	98.8	..	..

It is evident that as the temperature is increased, the extent of the oxidation of methyl alcohol, or the corresponding yields of hydrogen and carbonates, also increases in percentages commensurate with the stoichiometrical ratios required by summation Equation III.

The presence of methylates in the reaction residues from seven runs is evidence of the occurrence of reaction (1) noted in the reaction mechanism scheme. The presence of formates in the reaction residues from the first three runs, that is, at temperatures below 300°, indicates the occurrence of the intermediate reactions represented by equations (2), (4) and (5), summation of which with (1) gives Equation II. (Separate runs with formic acid showed its complete decomposition at 300° but accompanied with some carbonization.) Oxidation of methyl alcohol according to the final summation Equation III is 85% complete at 370° and 100% complete at 450°.

Incidentally, a note should be incorporated relative to methyl alcohol runs made with sodium hydroxide and with potassium hydroxide separately. This was in compliance with a request from Professor J. R. Withrow, Chairman of the Committee of the National Research Council on Substitution of Sodium Compounds for the Conservation of Potassium Compounds, that we test the effect of the alkalies separately.

Three groups of runs, each in duplicate, were made with 10 cc. or 7.89 g. of methyl alcohol, the first with 117 g. of potassium hydroxide, the second with 83 g. of sodium hydroxide, and the third with a mixture of 51.1 g. of potassium hydroxide and 55.3 g. of sodium hydroxide, which has a lower melting point (185°) than any other mixture. All runs were made at 450°. The data are embodied in Table II.

The yields of hydrogen and carbonates with potassium hydroxide and sodium hydroxide, separately, are approximately 95% of the theoretical and nearly identical, but for the mixture of alkalies they are practically theoretical. These experiments also show that by working at sufficiently high temperatures sodium hydroxide could be substituted for potassium

TABLE II

EFFECT OF THE CAUSTIC ALKALIES SEPARATELY AND MIXED, RUN I (KOH), RUN II (NAOH), RUN III (KOH AND NAOH)

Run	H_2 found, liters (0°/760 mm.)	H_2 calcd., eq. III	H_2, % of theory	CO_2 found, g.	CO_2 calcd., eq. III	CO_2, % of theory
Ia	16.1	16.6	96.7	9.32	10.82	86.0
Ib	15.6	16.6	93.7	10.23	10.82	94.4
IIa	16.0	16.6	96.2	10.56	10.82	97.4
IIb	15.9	16.6	95.2	9.82	10.82	91.6
IIIa	16.7	16.6	100.6	10.53	10.82	97.5
IIIb	16.5	16.6	99.4	10.85	10.82	100.2

hydroxide, but convenience in operation of this special method of conducting the reactions requires the use of a mixture, the fusion point of which is initially the lowest obtainable.

B. Ethyl Alcohol

When the type reaction mechanism is applied to ethyl alcohol, the following reactions are indicated

$$CH_3CH_2OH + NaOH \longrightarrow CH_3COONa + 2H_2 \qquad (8)$$
$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$
$$\Sigma\ (8), (9) \quad CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4 \qquad (10)$$

In previous runs with ethyl alcohol at 250–280°, Fry and Schulze[2b] obtained not only hydrogen, methane, acetates and carbonates, the products of reactions (8) and (9), but also much ethylene, arising presumably according to equation (11).

$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \qquad (11)$$

The incomplete interaction of ethyl alcohol at 250–280° and the simultaneous occurrence of reactions (8), (9) and (11) made it impossible in the earlier experiments to check the stoichiometrical ratios indicated and thereby establish the summation reaction, equation (10).

In these subsequent experiments, it has been found that runs made with 10 cc. (7.84 g.) portions of ethyl alcohol *at higher temperatures* gave lower yields of acetates, higher yields of carbonates, with hydrogen and methane approaching the relative volume ratio 2:1. In other words *as the temperature is raised, the reaction tends to conform to the summation*

TABLE III

ETHYL ALCOHOL DATA, 530°

	Run I	Run II		Run I	Run II
C_2H_5OH, g.	7.84	7.84	CH_4 calcd., liters (0°/760 mm.)	3.9	3.9
H_2 found, liters (0°/760 mm.)	7.8	8.2	CH_4 calcd., %	100	92
H_2 calcd., liters (0°/760 mm.)	7.9	7.9	Vol. ratio, H_2:CH_4	1.95:1	2.27:1
H_2 calcd., %	99	104	CO_2 found, g.	6.7	6.4
CH_4 found, liters (0°/760 mm.)	3.9	3.6	CO_2 calcd., g.	7.5	7.5
			CO_2 calcd., %	90	85

equation (*10*). This is clearly evident from the data of two duplicate runs (Table III) conducted at 530°. All calculations are based upon summation equation (10).

In this reinvestigation of the interaction of ethyl alcohol with fused caustic alkalies at higher temperatures, neither acetates nor ethylene were obtained; the quantitative data indicate practically complete oxidation of ethyl alcohol to carbonate with the liberation of hydrogen and methane in conformity with the proposed type reaction

$$CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4$$

C. Normal Propyl Alcohol

In view of this behavior of ethyl alcohol, it is natural to assume that normal propyl alcohol would react quite similarly to yield carbonates, hydrogen and ethane in conformity with the type equation (12)

$$CH_3CH_2CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + C_2H_6 \qquad (12)$$

Other equations, (13) and (14) following, indicating respectively more extensive and finally complete oxidation, may be derived by extending the type reaction to the other hydrogen atoms of the propyl alcohol molecule

$$CH_3CH_2CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + CH_4 + 5H_2 \qquad (13)$$

$$CH_3CH_2CH_2OH + 10NaOH \longrightarrow Na_2CO_3 + 2Na_4CO_4 + 9H_2 \qquad (14)$$

Equations (12), (13) and (14) represent three stages of oxidation of propyl alcohol by the fused caustic alkalies. To determine the actual extent of the oxidation, duplicate runs at 500° were made with 10 cc. or 8 g. portions of pure normal propyl alcohol according to the usual method. The alcohol reacted readily and completely, but the reaction residue, in addition to carbonates, was found to contain some free carbon. The gases evolved, collected and analyzed contained *no ethane* but *hydrogen* and *methane* in ratio by volume of about 4.3:1.

The absence of methane precludes the reaction noted in equation (12); the presence of methane and the hydrogen-methane gas volume ratio indicate equation (13) and preclude equation (14). The presence of some free carbon in the reaction residue precludes the establishment of exact stoichiometrical ratios for any assumed reaction, but the data obtained approximate most closely those ratios indicated in equation (13). Ac-

TABLE IV

NORMAL PROPYL ALCOHOL DATA, 500°

	Run I	Run II		Run I	Run II
C_3H_7OH, g.	8.0	8.0	CH_4 calcd., liters (0°/760 mm.)	2.7	2.7
H_2 found, liters (0°/760 mm.)	11.9	10.4	CH_4 calcd., %	92.7	100.0
H_2 calcd., liters (0°/760 mm.)	14.6	14.6	Vol. ratio, H_2:CH_4	4.75:1	3.9:1
H_2 calcd., %	81.5	73.8	CO_2 found, g.	8.79	8.26
CH_4 found, liters (0°/760 mm.)	2.5	2.7	CO_2 calcd., g.	11.7	11.7
			CO_2 calcd., %	75.1	70.6

cordingly, for convenience of record and comparison, all of the quantitative data which follow in Table IV are based upon the stoichiometrical requirements of equation (13), which is apparently the dominant reaction occurring at 500°.

D. Isopropyl Alcohol

Since ethyl and normal propyl alcohols are oxidized by fused caustic alkalies to carbonates with the liberation of hydrogen and methane, it is naturally assumed that *iso*propyl alcohol will also react similarly according to the proposed type equation (15)

$$(CH_3)_2CHOH + 2NaOH \longrightarrow Na_2CO_3 + H_2 + 2CH_4 \qquad (15)$$

This assumption has been verified by the quantitative data obtained in duplicate runs at 500° with 20 cc. or 15.7 g. quantities of pure *iso*propyl alcohol. The sole products of the reactions were carbonates, hydrogen and methane, with very minute traces of free carbon in the reaction residue. The yields of the products, as recorded in Table V, are calculated in terms of the stoichiometrical ratios required by equation (15).

TABLE V

*Iso*PROPYL ALCOHOL DATA, 500°

	Run I	Run II
$(CH_3)_2CHOH$, g.	15.7	15.7
H_2 found, liters (0°/760 mm.)	11.5	11.3
H_2 calcd., liters (0°/760 mm.)	11.5	11.5
H_2 calcd., %	100.0	98.3
CH_4 found, liters (0°/760 mm.)	5.7	5.5
CH_4 calcd., liters (0°/760 mm.)	5.8	5.8
CH_4 calcd., %	98.2	95.6
Vol. ratio, H_2:CH_4	1:2.04	1:2.05
CO_2 found, g.	10.94	10.84
CO_2 calcd., g.	11.40	11.40
CO_2 calcd., %	96.0	95.1

The above data confirm, within the limits of experimental error entailed in the method, the stoichiometrical ratios, $(CH_3)_2CHOH:CO_2:H_2:2CH_4$, required by the assumed type equation (15).

E. Isobutyl Alcohol

The three carbon chain compound, normal propyl alcohol, underwent some carbonization on interaction with the fused caustic alkalies, while ethyl and *iso*propyl alcohols, two carbon chain compounds, suffered little if any carbonization. It was accordingly expected that runs with *iso*butyl alcohol, a three carbon chain compound, would also be impaired by some carbonization. In fact, two runs with *iso*butyl alcohol, one at 350° and one at 500°, were accompanied by such extensive carbonization that *results possessing any stoichiometrical significance could not be obtained.*

F. Tertiary Butyl Alcohol

In view of the facts just noted, the isomer of *iso*butyl alcohol, namely the two carbon chain compound, tertiary butyl alcohol, should react with the fused caustic alkalies with little or no carbonization and yield carbonates and methane in conformity with the proposed type equation (16).

$$(CH_3)_3COH + 2NaOH \longrightarrow Na_2CO_3 + 3CH_4 \qquad (16)$$

To verify this equation, duplicate runs made at 500° with weighed samples of pure tertiary butyl alcohol gave reaction residues containing carbonates *free from carbon.* The gas evolved, as predicted, was chiefly methane but contained some hydrogen, undoubtedly a by-product of some minor secondary reaction, since the ratio by volume of methane to hydrogen was 24:1. Some of the tertiary butyl alcohol escaped interaction: it distilled unaffected through the fused alkalies, was condensed, recovered, weighed and deducted from the initial amount used. The yields of methane and carbonates, as recorded in Table VI, are calculated in terms of the stoichiometrical ratios required by equation (16).

TABLE VI

TERTIARY BUTYL ALCOHOL DATA, 500°

	Run I	Run II		Run I	Run II
$(CH_3)_3COH$, g.	14.4	11.8	CH_4 calcd., %	87.4	91.9
CH_4 found, liters (0°/760 mm.)	11.2	9.6	CO_2 found, g.	7.43	6.07
CH_4 calcd., liters (0°/760 mm.)	12.8	10.4	CO_2 calcd., g.	8.51	6.93
			CO_2 calcd., %	87.3	87.6

The yields of methane and carbonates are in conformity with the stoichiometrical ratio, $(CH_3)_2COH:3CH_4:CO_2$, required by the assumed type equation (16).

G. Methyl Formate

The interaction of methyl formate with the fused caustic alkalies may be assumed to involve three principal reactions. The first, equation (17), is the saponification of methyl formate yielding formate and methyl alcohol

$$HCOOCH_3 + NaOH \longrightarrow HCOONa + CH_3OH \qquad (17)$$

The second, equation (18), is the type reaction for the oxidation of formate to carbonate with liberation of hydrogen

$$HCOONa + NaOH \longrightarrow Na_2CO_3 + H_2 \qquad (18)$$

The third, equation (19), is the summation Equation III, previously developed and verified again in Section A, indicating complete oxidation of methyl alcohol to carbonate with evolution of hydrogen

$$CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2 \qquad (19)$$

The summation of equations (17), (18) and (19) gives equation (20) which is the assumed reaction for the complete oxidation of methyl formate

$$HCOOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2 \qquad (20)$$

To test the validity of this assumption (that is, equation 20), several runs were made with pure methyl formate, which, on account of its low boiling point (32°) could not be introduced into the tube bearing the fused alkalies in the customary manner directly from a Walther dropping funnel. The methyl formate (about 10 cc.) was first introduced into a weighed gas liquefying bulb with inlet and outlet stopcocks. The outlet stopcock was connected by glass tubing to the apparatus containing the fused alkalies. Opening of the exit cock and gentle warming of the gas liquefying bulb permitted a steady flow of methyl formate vapor through the caustic alkalies, which were maintained at 475°. Reweighing of the tube after vaporization of its contents gave the weight of methyl formate used.

Reaction took place readily in each of the three runs. The gas evolved was pure hydrogen. The reaction residue contained the carbonates *with some free carbon. (When separate runs were made with formic acid, free carbon was likewise formed.)* The quantitative data are noted in Table VII. The calculations are based upon the previously developed summation equation (20).

TABLE VII

METHYL FORMATE DATA, 475°

Run	HCO_2CH_3 g.	H_2 found, liters (0°/760 mm.)	H_2 calcd., liters (0°/760 mm.)	H_2 calcd., %	CO_2 found, g.	CO_2 calcd., g.	CO_2 calcd., %
I	6.57	8.0	9.8	81.5	8.1	9.6	71.1
II	8.62	11.1	12.9	86.2	10.1	12.6	70.6
III	8.23	10.1	12.3	82.3	9.7	12.1	70.0

In these runs with methyl formate, the yields of hydrogen, based on equation (20), are ten or more per cent. greater than the corresponding yields of carbonate. Nevertheless, the data show that at least 70% of the methyl formate was oxidized to carbonate with the liberation of hydrogen in conformity with the assumed type reaction equation (20).

H. Methyl Acetate

The extended application of the type reactions to methyl acetate leads directly to equations which are exactly parallel to those proposed for methyl formate. In other words, the following equations (21), (22), (23) and (24) are, respectively, similar to the previously proposed equations, (17), (18), (19) and (20).

$$CH_3COOCH_3 + NaOH \longrightarrow CH_3COONa + CH_3OH \qquad (21)$$

$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (22)$$

$$CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2 \qquad (23)$$

$$(21),\ (22),\ (23)\quad CH_3COOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + CH_4 + 3H_2 \qquad (24)$$

The extent to which this summation equation (24) has been verified is shown by the quantitative data of duplicate runs with 9.28 g. samples of pure methyl acetate made at 475° and recorded in Table VIII. The reaction residues contained carbonates but no free carbon. The gases evolved were hydrogen and methane.

TABLE VIII

METHYL ACETATE DATA, 450°

	Run I	Run II
CH_3COOCH_3, g.	9.28	9.28
H_2 found, liters (0°/760 mm.)	9.01	9.02
H_2 calcd., liters (0°/760 mm.)	8.44	8.44
H_2 calcd., %	106.7	106.8
CH_4 found, liters (0°/760 mm.)	2.58	2.78
CH_4 calcd., liters (0°/760 mm.)	2.79	2.79
CH_4 calcd., %	92.2	99.6
Vol. ratio, $H_2:CH_4$	3.37:1	3.24:1
CO_2 found, g.	9.57	9.79
CO_2 calcd., g.	11.03	11.03
CO_2 calcd., %	86.8	88.7

While the checks for the yields of the several products of the reaction are in fair agreement, there are certain deviations from the stoichiometrical ratios ($CH_3COOCH_3:3H_2:CH_4:2CO_2$) required by the summation equation (24) which call for further comment.

The excessive yields of hydrogen over methane and carbonates indicate some further oxidation of the methyl radical or methane not accounted for in equation (24). The yield of carbonates is nearly 88% of the theoretical. This indicates that, notwithstanding the excessive yields of hydrogen, about 88% of the methyl acetate was oxidized to carbonate in conformity with the proposed summation equation (24).

Other investigations, runs similar to those described, were made with the following compounds: ammonia, monomethyl-, dimethyl- and trimethyl- amines and dimethyl and diethyl ether. In each case, *there was no evidence obtained indicating the occurrence of any chemical change whatsoever.* In other words, the vapors of the compounds noted resisted the oxidizing action of the fused caustic alkalies.

It is again a pleasure to express our appreciation of the continued interest of Dr. Ernst Twitchell, the donor of the graduate fellowship stipends which have made the continuation of the work described in this and the two following papers possible.

Summary

The special method, apparatus and hypothesis suggested for the mechanism of the reactions, investigated quantitatively as described in previous papers,[2] have been extended to a further investigation of the behavior of methyl and ethyl alcohols, and to initial studies of the behavior of normal propyl, *iso*propyl, *iso*butyl and tertiary butyl alcohols, and to the simple esters, methyl formate and methyl acetate.

With methyl alcohol further evidence has been adduced through duplicate series of runs extending over a wide range of temperatures, 250–450°, confirming certain intermediate reactions assumed to occur according to the proposed type equation

$$RH_n + n\ MOH \longrightarrow R(OM)_n + n\ H_2\ (M = Na \text{ or } K)$$

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 stoichlometric 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]

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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).