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

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS

II. THE INTERACTION OF ETHYL ALCOHOL, ACETALDEHYDE AND ACETONE WITH FUSED CAUSTIC ALKALIES

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Introduction

In article I of this series[2] an hypothesis was proposed to explain the liberation of hydrogen from carbon compounds and their concomitant oxidation when their vapors were passed through *fused, anhydrous*, equimolar mixtures of sodium and potassium hydroxides. It was assumed that these reactions involved *the acidic dissociation of the alkalies* and conformed to a general type reaction (M = Na or K): $R(H)_n + n\text{HOM} \longrightarrow R(\text{OM})_n + nH_2$.

In a study of this type reaction in its relation to (1) methyl alcohol and (2) formaldehyde, evidence was adduced substantiating quantitatively the occurrence of the following reactions.

$$CH_3OH + 2MOH \longrightarrow M_2CO_3 + 3H_2 \qquad (1)$$

$$CH_2O + 2MOH \longrightarrow M_2CO_3 + 2H_2 \qquad (2)$$

The stoichiometrical ratios (1) $CH_3OH{:}CO_2{:}3H_2$ and (2) $CH_2O{:}CO_2{:}2H_2$, were established.

It is proposed in the present study to investigate further the type reaction, and the suggested mechanism, by extending the previously described special method of conducting these reactions to ethyl alcohol, acetaldehyde and acetone.

In the early history of organic chemistry frequent observations were recorded on the liberation of hydrogen from carbon compounds when heated in glass tubes or retorts with soda lime, potash lime, caustic alkalies or barium hydroxide. Most of these experiments were qualitative rather than quantitative and in no instances, as far as we are able to ascertain, were the reactions conducted in the manner described in our previous paper, namely, by passing the vapors of the *pure anhydrous carbon compounds* through *fused anhydrous caustic alkalies*. A few references to earlier observations, however, are now pertinent, especially in their bearing upon the question of the mechanism of the reactions.

Dumas and Stas,[3] advocating the "older type theory," maintained 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

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[1] Summary of a section of the doctorate research of Else L. Schulze.

[2] Fry, Schulze and Weitkamp, THIS JOURNAL, **46**, 2268 (1924).

[3] Dumas and Stas, *Ann.*, **35**, 129 (1840).

hydrogen which comes jointly from the water and the carbon compound. Thus when ethyl alcohol is heated with lime and potassium hydroxide, acetates and hydrogen are formed. Dumas' statement of this reaction translated into modern formulas is $C_2H_6O + H_2O \longrightarrow C_2H_4O_2 + 2H_2$. Dumas and Stas similarly converted (qualitatively) cetyl alcohol to palmitic acid; acetaldehyde to acetate and hydrogen; and acetone to carbonates (no acetates) with the liberation of hydrogen and methane.

Many of the experiments described by Dumas and Stas were repeated and others of similar character performed by Lewy,[4] Löwig,[5] Brodie[6] and Gerhardt.[7] Precise stoichiometrical relationships between the quantities of the interacting compounds and the products formed were not established, but the later work of Carl Hell[8] is more significant stoichiometrically since he proposed to determine the molecular weights of the higher alcohols by measuring the quantity of hydrogen evolved in conformity with the reaction, $R.CH_2OH + NaOH \longrightarrow R.CO_2Na + 2H_2$. Hell heated 0.5 to 1.0-g. 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 yields obtained were from 80 to 85%. He 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, because other complex decompositions were encountered.

Reference must now be made to the work of Maitland C. Boswell and J. V. Dickson[9] on the action of fused alkali on organic and inorganic compounds which we failed to note[10] in our first paper. These authors[11] state: "The working hypothesis which had been devised by the senior author to assist in the main investigation, indicated the probability that in such fusion the elements of water are active, and that oxidations might be possible whose mechanism would consist of a decomposition of water, the oxygen being taken up by the sodium arsenite or other oxygen acceptor present, and the hydrogen evolved in the free state." Again,[12] "The mechanism of these reactions consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation and the hydrogen being evolved in the gaseous state." It

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[4] Lewy, *Ann. chim. phys.*, [3] **13**, 439 (1845).

[5] Löwig, "Chem. org. Verbind.," Friedrich Vieweg und Sohn, Braunschweig, **1846**, p. 278.

[6] Brodie, *Ann.*, **67**, 180 (1848); **71**, 149 (1849).

[7] Gerhardt, *Ann. chim. phys.*, [3] **15**, 236 (1845).

[8] Hell, *Ann.*, **223**, 269 (1884).

[9] Boswell and Dickson, THIS JOURNAL, **40**, 1773, 1779, 1786 (1918).

[10] Dickson, *ibid.*, **47**, 2061 (1925).

[11] Ref. 9, p. 1773.

[12] Ref. 9, p. 1778.

should be noted that this hypothesis was originally proposed by Dumas and Stas in 1840 and extensively employed by them and others.

Some such reactions may virtually involve the decomposition of water but we are inclined more strongly to the hypothesis that the mechanism of these reactions involves primarily the acidic dissociation of the alkali hydroxides and conforms to the type reaction $R(H)_n + nHOM \longrightarrow R(OM)_n + nH_2$. In fact, as previously shown,[13] *anhydrous* formaldehyde generated by the depolymerization of trioxymethylene, passed through an *anhydrous* fused equimolar mixture of sodium and potassium hydroxides at 300–325°, is transformed *quantitatively* (90%) in conformity with the type reaction, $OCH_2 + 2HOM \longrightarrow OC(OM)_2 + 2H_2$.[14]

B. H. Carroll,[15] on the basis of a noteworthy quantitative investigation of the action of the vapors of absolute ethyl alcohol and of acetaldehyde upon soda lime, concluded that sodium hydroxide functioned both as a catalyst and as an active reagent. "The reason for using soda lime instead of caustic soda is that the latter is a liquid at the temperature involved and is hard to handle."

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[13] Ref. 2, p. 2274.

[14] Experimental evidence also leads us to take exception to the claim of Boswell and Dickson (Ref. 9, p. 1787) to which our attention has recently been called by Dickson (Ref. 10, p. 2062) that "resorcinol 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." This observation is contradicted by the following experiment conducted in our Laboratory: 0.01 mole (1.1 g.) of resorcinol on decomposition by fusion in a Jena glass tube with 4 g. of an equimolar mixture of sodium and potassium hydroxides yielded, *without any access whatsoever to oxygen, 796 cc. of hydrogen (standard conditions).* This quantity is 88.84% of the theoretical yield of all of the hydrogen available in resorcinol according to our type reaction. This difference in results may be explained by citing the data of two experiments, (*a*) and (*b*), which show that conditions other than the previous heating of resorcinol with access to oxygen determine the liberation of hydrogen. (*a*) Boswell and Dickson (Ref. 9, p. 1788) heated 0.5 g. of resorcinol with 2 g. of sodium hydroxide for 40 minutes at 350° and obtained only 0.4 cc. of hydrogen. (*b*) Fry and Schulze heated 0.55 g. of resorcinol (1/200 mole) with 2 g. of an equimolar mixture of sodium and potassium hydroxides in a tube which had been filled with hydrogen so as 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 (under standard conditions) was 598 cc. of which 407 cc. was hydrogen plus some hydrocarbon and a trace of carbon monoxide. This yield of hydrogen was 90.85% of that calculated for all of the available hydrogen of resorcinol according to the type reaction, $C_6H_4(OH)_2 + 6MOH \longrightarrow C_6(OM)_6 + 2H_2O + 4H_2$. The reaction residue was not identified as $C_6(OM)_6$ but chiefly as decomposition products, namely, alkali carbonates and free carbon. Alkalimeter determinations gave 0.5406 g. of CO_2 which is 40.96% of that calculated for all the carbon in resorcinol.

It is thus evident that higher and longer heating of resorcinol with mixed alkalies gives almost calculated yields of hydrogen, the evolution of which is not dependent upon previous heating with access to oxygen.

[15] Carroll, *J. Phys. Chem.*, **22**, 128 (1918).

Carroll's data on hydrogen, methane and acetate determinations substantiate to a limited extent the equations for the following reactions which are commonly assumed to occur.

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CO_2Na + 2H_2$$
$$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$$

When he passed ethyl alcohol vapor over small amounts (2 to 7 g.) of sodium hydroxide, the loss by spattering, etc., was so great "that altogether no quantitative determination of acetate formation could be made." In no instances did Carroll indicate the quantity of carbonate formed which is equally as important as the acetate.

Concerning the mechanism of the reaction, Carroll states:

> "The conversion of alcohol to acetate in presence of soda lime takes place in at least three stages. The first stage is the dissociation of alcohol to aldehyde and hydrogen in the presence of caustic soda as catalytic agent, $CH_3CH_2OH = CH_3CHO + H_2$.
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> "Aldehyde is found in the liquid products when caustic soda is used."......"The second stage......is the dissociation of aldehyde presumably to ketene and hydrogen in presence of caustic soda as catalytic agent according to the equation $CH_3CHO = CH_2CO + H_2$.
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> "The intermediate formation of ketene has not been shown; but it is the most probable reaction and it does not seem probable that aldehyde splits off one atom of hydrogen, forming temporarily the free acetyl group. The third stage in the reaction is the combination of ketene with caustic soda to form sodium acetate according to the equation $CH_2CO + NaOH \longrightarrow CH_3CO_2Na$."

Apropos of this review, our assumption that these reactions involve primarily the acidic dissociation of the alkali hydroxides and the proposed type reaction[16] appears to be substantiated further by the present study of the reactions which occur when the vapors of (A) absolute ethyl alcohol, (B) acetaldehyde and (C) acetone are bubbled through a large excess of a fused anhydrous equimolar mixture of sodium and potassium hydroxides. The special apparatus and experimental procedure are the same as described in our previous paper.

A. Ethyl Alcohol

In extending the type reaction, $R(H)_n + nHONa;\ R(ONa)_n + nH_2$, to ethyl alcohol, as was previously done with methyl alcohol, the hydrogen atoms of the CH_2OH radical would naturally be the first susceptible to replacement. The partial type reactions may be indicated and summarized as follows.

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2O \qquad (3)$$
$$CH_3CH_2ONa + HONa \longrightarrow CH_3CH(ONa)_2 + H_2 \qquad (4)$$
$$CH_3CH(ONa)_2 + HOH \longrightarrow CH_3CHO + 2NaOH \qquad (5)$$
$$\Sigma\ (3),\ (4),\ (5)\ CH_2CH_2OH \longrightarrow CH_3CHO + H_2 \qquad (6)$$

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[16] The theories of J. U. Nef [*Ann.*, **318**, 137 (1901)] on the dissociation of monatomic alcohols may be of interest in this connection, but do not bear directly upon our proposed reaction mechanism. The catalytic dehydration of alcohol, investigated by R. N. Pease and Chi Chao Yung [THIS JOURNAL, **46**, 390, 2397 (1924)], may also be noted.

This reaction, summation of consecutive type reactions 3, 4 and 5, affords an explanation of the mechanism of the reaction for the formation of acetaldehyde. Carroll[15] showed that some acetaldehyde was a by-product in the reaction between alcohol and sodium hydroxide. Its formation undoubtedly precedes that of sodium acetate which then conforms to the next type reaction 7,

$$CH_3CHO + HONa \longrightarrow CH_3CO(ONa) + H_2 \qquad (7)$$

The summation of Reactions 3, 4, 5 and 6 gives the familiar reaction 8,

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CO_2Na + 2H_2 \qquad (8)$$

The conversion of sodium acetate to carbonate, with the liberation of methane, then follows according to type reaction 9,

$$CH_3CO_2Na + HONa \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$

It is significant that this proposed type-reaction mechanism does not necessitate Carroll's assumption that "the second stage is the dissociation of aldehyde presumably to ketene and hydrogen in the presence of caustic soda as catalytic agent according to the equation $CH_3CHO = CH_2CO + H_2$," and that the third stage is the union of ketene with sodium hydroxide to form acetate, $CH_2CO + NaOH = CH_3CO_2Na$. In fact, as Carroll has stated, "the intermediate formation of ketene has not been shown."

Furthermore, it is here suggested that 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 10,

$$CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2 \qquad (10)$$

This reaction (10) will serve to explain the excessive yield of hydrogen formed over that required by the theory according to Reaction 8.

Ethylene was also formed in the gases evolved, due to the catalytic decomposition of ethyl alcohol at temperatures employed by the alkalies present according to Reaction 11,

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

The principal products formed when ethyl alcohol vapor was passed through the fused alkalies at 250°, quantities of which were subsequently determined, are thus accounted for by the following reactions, mechanisms of which have been indicated.

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CO_2Na + 2H_2 \qquad (8)$$
$$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$
$$CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2 \qquad (10)$$
$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \qquad (11)$$

Since these reactions are simultaneous and independent, it is not possible to obtain quantitative data establishing completely the stoichiometrical ratios between the yields of acetate, carbonate, hydrogen and ethylene. Nevertheless, the data of two typical experimental runs herewith presented substantiate in some measure the type reactions noted.

In each run, 50cc. samples of absolute ethyl alcohol were vaporized and bubbled slowly (8–12 hours) through an equimolar mixture of fused anhydrous sodium and potassium hydroxides maintained at temperature 250–280°, according to the method of procedure described in a previous communication.[2] About 30 cc. of distillate was collected. It consisted chiefly of undecomposed ethyl alcohol. Since the boiling-point range of this distillate ran from 78° to 195°, the exact quantity of ethyl alcohol entering into the reaction was not determined. (Methyl alcohol, under similar conditions, reacted completely.)

Many aliquot samples of the total volumes of gases evolved were analyzed according to standard methods and the total quantities of hydrogen, methane and ethylene formed were calculated. The total yields of acetates and carbonates were determined by applying standard methods of analysis to aliquot portions of the reaction residues. The acetates (liberated and titrated as acetic acid) and the carbonates (alkalimeter determinations) were calculated as acetic acid and carbon dioxide, respectively.

In Table I, which summarizes the analytical data of two runs, the percentage of the calculated yield of hydrogen is based upon the amount of acetate formed according to Reaction 8, in terms of the stoichiometrical ratio $CH_3CO_2H:2H_2$. The percentage of the calculated yield of methane is based upon the carbonates formed in Reaction 9, and its ratio $CO_2:CH_4$. The percentage of the calculated yield of the ethylene formed according to Reaction 11 is not calculable since no product therefrom occurs in the reaction residue.

TABLE I

ETHYL ALCOHOL DATA

The volumes of gases are reduced to standard conditions

Run	CH_3CO_2H found, g.	H_2 found, liters	H_2 calcd., liters	Calcd., %
I	7.40	6.16	5.53	111.40
II	3.49	2.71	2.61	103.83
	CO_2 found, g.	CH_4 found, liters	CH_4 calcd., liters	Calcd., %
I	1.17	0.086	0.596	14.43
II	1.37	.030	.699	4.30
	C_2H_4 found, liters			
I	3.37			
II	3.88			

Since more than a 100% yield of hydrogen was obtained, based upon the ratio $CH_3CO_2H:2H_2$ of Reaction 8, the conclusion is warranted that some other reaction yielding hydrogen occurred. In terms of the proposed mechanism, this reaction would probably be No. 10 which involves all of the hydrogen atoms of the ethyl alcohol molecule and indicates the ratio

$CO_2:3H_2$. This explanation is supported further by the fact that the yields of carbonates are in excess of that of methane according to the ratio $CO_2:CH_4$ called for by Reaction 9, and that the corresponding yields of methane are very low. In other words, Reaction 9 proceeds to a very limited extent and the source of the hydrogen is not only Reaction 8 but also quite likely Reaction 10.

The comparatively large yields of ethylene indicate the extensive occurrence of Reaction 11, for which, as previously explained, no stoichiometrical ratios are here available.

In similar runs at higher temperature, 300–320°, the same gaseous and solid products were obtained but not in stoichiometrical ratios. Relatively more methane was produced than in the lower temperature runs.

B. Acetaldehyde

It is significant that the formation of acetaldehyde follows *a priori* from the application of the proposed type-reaction mechanism hypothesis to ethyl alcohol. (See Reaction 6, the summation of type reactions 3, 4 and 5, in Section A.) Only traces of aldehyde are recoverable as a product of the reaction because it is immediately converted into acetate and hydrogen according to the consecutive type reaction 7,

$$CH_3CHO + HONa \longrightarrow CH_3CO(ONa) + H_2 \qquad (7)$$

In turn the acetate is transformed into carbonate and methane through type reaction 9,

$$CH_3CO_2Na + HONa \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$

Finally, Reaction 12, the summation of Reactions 7 and 9, indicates the conversion of aldehyde to carbonate, hydrogen and methane.

$$CH_3CHO + 2NaOH \longrightarrow Na_2CO_3 + H_2 + CH_4 \qquad (12)$$

Accordingly, the object of the experiments with acetaldehyde is to determine the conditions under which and the extent to which the foregoing Reactions 7, 9 and 12 take place. The practically complete interaction of acetaldehyde with the fused caustic alkalies facilitates this object.

Three runs, I, II and III, were conducted with acetaldehyde (of checked purity) at respective temperatures 250°, 300° and 350°. In each the yields of hydrogen, methane and carbonate were determined as previously described. Acetate determinations were made only in Run I in which the aldehyde reacted almost completely according to Reaction 7. They were neither made nor required in connection with Runs II and III because practically complete conversion of the aldehyde to hydrogen, methane and carbonates took place according to Reaction 12. The gases evolved contained neither carbon monoxide nor unsaturated hydrocarbons. The experimental data are summarized in Table II.

In Run I, acetaldehyde interacted completely with excess of caustic alkalies at 250° and gave more than 90% yields of hydrogen and acetates.

Table II

Acetaldehyde Data

I (250°); II (300°); III (350°)

The volumes of gases are reduced to standard conditions

Run	CH_3CHO, g.	H_2 found, liters	H_2 calcd., liters	Calcd., %
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 found, liters	CH_4 calcd., liters	Calcd., %
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 found, g.	CO_2 calcd., g.	Calcd., %
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 found, g.	CH_3CO_2H calcd., g.	Calcd., %
I	15.75	20.37	21.4	95.19
II	15.35	...	...	...
III	15.75	...	...	...

This indicates that the reaction conformed within the limits of the experimental conditions to the stoichiometrical ratios required by Reaction 7, $CH_3CHO + NaOH \longrightarrow CH_3CO_2Na + H_2$. Since very small yields of methane and corresponding carbonates were obtained, Reaction 9, $CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$, took place to a commensurate extent.

On the other hand, in Runs II and III at 300° and 350°, respectively, the yields of hydrogen, methane and carbonates are practically theoretical for the summation of consecutive reactions 7 and 9, namely, Reaction 12, $CH_3CHO + 2NaOH \longrightarrow H_2 + CH_4 + Na_2CO_3$. (The slightly lower yield of carbonates, 86.73%, may be explained by the physical difficulties encountered in completely recovering all of the solidly fused reaction mixture from the iron tubes in which the reaction took place.)

C. Acetone

The literature, as previously noted, records the formation of a variety of products when acetone reacts with soda lime but gives no account of the yields of the products when acetone vapors are bubbled slowly through an excess of an equimolar mixture of fused caustic alkalies in the special manner employed in this investigation.

Since acetone is structurally similar to acetaldehyde it is natural to assume that its interaction with the alkalies would conform to the preceding type reactions 7, 9 and 12 shown by acetaldehyde. Analogously, the type reactions for acetone, 13, 9 and 14, the latter being the summation of the two preceding, are as follows.

$$CH_3COCH_3 + NaOH \longrightarrow CH_3CO_2Na + CH_4 \qquad (13)$$
$$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$
$$CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4 \qquad (14)$$

To check these assumptions and reactions quantitatively, two sets of experiments, Run IV at 250° and Run V at 350°, were conducted with acetone of determined purity.

At 250°, methane was the principal gas evolved with a small amount of hydrogen (1.57 liters, 0°/760 mm.) and ethylene (0.297 liter, 0°/760 mm.), and only traces of carbon monoxide. The reaction residue consisted chiefly of acetates with some carbonates.

At 350°, the volume of methane was more than doubled. It contained little hydrogen (1.16 liters, 0°/760 mm.), no ethylene 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 the calculated yields and percentage yields calculated on the basis of Reaction 13 and 14. Since only a few drops, practically non-weighable quantities, of liquid possessing the characteristic odor of acetone condensation products were collected in each run, all calculations were based upon the original amounts of acetone used.

TABLE III

ACETONE DATA

IV (250°); V (350°)

The volumes of gas are reduced to standard conditions

Run	$(CH_3)_2CO_2$ g.	CH_4 found, liters	CH_4 calcd. (Reac. 13) liters	CH_4 calcd. (Reac. 13), liters, %	CH_4 calcd. (Reac. 14), liters	CH_4 calcd. (Reac.14), liters, %
IV	19.75	5.41	7.63	70.91	15.26	35.46
V	19.98	14.27	...	...	15.44	92.43

Run	$(CH_3)_2CO$, g.	CH_3CO_2H found, g.	CH_3CO_2H calcd. (Reac. 13), g.	CH_3CO_2H calcd. (Reac. 13), %
IV	19.75	17.33	20.44	84.79
V	19.98	none	none	none

Run	$(CH_3)_2CO$, g.	CO_2 found, g.	CO_2 calcd., g.	CO_2 calcd., %
IV	19.75	3.32	14.99	22.15
V	19.98	13.94	15.16	91.96

In drawing conclusions from the data of Table III it should be noted that the yields of methane may originate in Reactions 13 and 9, or in their summation reaction 14. However, in Run IV the 84.79% yield of acetate and the corresponding, but somewhat lower yield, 70.91%, of methane, are fairly commensurate with the stoichiometrical ratio, $CH_3CO_2H:CH_4$, required by Reaction 13. The solubility of methane in water, large volumes of which were necessarily present in collecting the gases, may explain its low yield in comparison to the acetate yield. The data indicate that, at 250°, at least 70% of the acetone used reacted with the alkalies according to Reaction 13, $CH_3COCH_3 + NaOH \longrightarrow CH_3CO_2Na + CH_4$.

On the other hand, in Run V, the 91.96% yield of carbonates (calculated as carbon dioxide) and the corresponding 92.43% yield of methane are quite commensurate with the stoichiometrical ratio, $CO_2:2CH_4$, required by Reaction 14. This indicates that at least 90% of the acetone used reacted with the fused alkalies at 350° in conformity with Reaction 14: $CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$.[17]

It is again a pleasure to express our gratitude for additional grants from Dr. Ernst Twitchell of graduate fellowship stipends which ensure the further investigation of the type reactions by Miss Else L. Schulze.

Summary

The special method, apparatus and hypothesis suggested for the mechanism of the reactions investigated quantitatively in the previous article[2] have been extended to the interactions taking place when the vapors of ethyl alcohol, acetaldehyde and acetone are bubbled through an excess of an equimolar mixture of fused caustic alkalies.

These changes may be readily explained in terms of an apparently general type reaction (M = Na or K), $R(H)_n + nMOH \longrightarrow R(OM)_n + nH_2$, which involves the acidic dissociation of the alkalies, the ultimate oxidation of the carbon compound to carbonate and the liberation of hydrogen. Similar type reactions explain the intermediate formation of acetates and methane.

The equations for the reactions with ethyl alcohol, aldehyde and acetone follow *a priori* from the application of the proposed type-reaction mechanism and they are validated by the quantitative results obtained.

Ethyl Alcohol.—The incomplete reaction of ethyl alcohol at temperatures of 250° and 300° 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.

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

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[17] The liberation of small amounts of hydrogen in the acetone runs is not accounted for by Reactions 13, 9 or 14, but if the type reaction should involve any of the hydrogen atoms of the methyl radicals, the production of hydrogen may thereby be readily explained. For example, the complete oxidation of acetone to carbonate and orthocarbonate may be represented by the type reaction, $CH_3COCH_3 + 10NaOH \longrightarrow Na_2CO_3 + 2Na_4CO_4 + 8H_2$. This is analogous to Reaction 10, under ethyl alcohol, $CH_3CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2$, which served to explain the excess yield of hydrogen over that required by Reaction 8. This explanation is receiving direct confirmation in experiments now under way with propionaldehyde which gives yields of hydrogen far in excess of that required by the analogous type reaction 7 under acetaldehyde.

Acetaldehyde.—Acetaldehyde reacted completely with the fused alkalies at 250°, hydrogen and acetates were the products of the reaction which conformed to the extent of 90% of the calculated amount to the reaction,

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

At 300° and 350° the yields of hydrogen, methane and carbonates were practically those calculated for the reaction,

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

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 calculated amounts, to the reaction,

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

At 350°, the yields of methane and carbonates were more than 90% of those calculated for the reaction,

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

Further applications of this special method of investigating the interactions between carbon compounds and fused caustic alkalies are in progress.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 506]

A METHOD FOR THE DIRECT IDENTIFICATION OF RAPESEED OIL BY ISOLATION OF ERUCIC ACID

BY ARTHUR W. THOMAS AND MORRIS MATTIKOW

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The purpose of this investigation was to find a method for the direct identification and quantitative estimation of rapeseed oil, the most important of the oils of the general order of *Cruciferae*, by isolating its characteristic acid, erucic acid. The isolation and purification of this acid is described in the literature.[1]

There was no attempt to separate or measure quantitatively erucic acid in rapeseed oil until 1910, when Tortelli and Fortini[2] and Holde and Marcusson[3] proposed their methods.

The method of Tortelli and Fortini depends on the determination of the iodine number and melting point of the fatty acids whose lead soaps are insoluble, or nearly so, in ether and on the critical temperature of solution

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[1] Darby, *Ann. chim. pharm.*, **69**, 1 (1849). Websky, *Jahresber.*, **6**, 443 (1853). Städeler, *Ann.*, **87**, 133 (1853). Otto, *Ann.*, **127**, 182 (1863). Hausknecht, *Ann.*, **143**, 41 (1867). Fitz, *Ber.*, **4**, 442 (1871). Farnsterner, *Z. Nahr. Genussm.*, **2**, 1 (1899). Reimer and Will, *Ber.*, **19**, 3320 (1886).

[2] Tortelli and Fortini, *Chem.-Ztg.*, **34**, 690 (1910).

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