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UNIVERSITY OF CINCINNATI

May 15 1931

I hereby recommend that the thesis prepared under my supervision by Richard A. Baltzly *entitled* The Oxidizing Action of Fused Anhydrous Caustic Alkalis upon Carbon Compounds. *be accepted as fulfilling this part of the requirements for the degree of* Ph.D.

Approved by:

H. Shipley Fry

W. M. Burgess, Chairman

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THE OXIDIZING ACTION OF FUSED ANHYDROUS CAUSTIC ALKALIES UPON CARBON COMPOUNDS

A dissertation submitted to the

Graduate School

of the University of Cincinnati

in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

1 9 3 1

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TABLE OF CONTENTS

I. INTRODUCTION

The reactions of fused caustic alkalies with carbon compounds find their most extensive applications in the aromatic series. Especially important are the conversion of aromatic sulfonic acids to phenols and the production of di- and tri- hydroxy benzene compounds by this method. Alkali fusions have also occupied an important field of application in the formation and production of various dyestuffs. In the majority of these reactions the importance is attached simply to the nature of the products formed with little question as to the mechanism of the reactions involved.

Beginning in 1922 investigations have been carried out by Fry and his coworkers (1,2,3,4,5,6) on the interaction of fused anhydrous caustic alkalies upon several classes of carbon compounds, all in the aliphatic series, in an attempt to explain the mechanism of the oxidation reactions, accompanied by the liberation of hydrogen and methane, in which caustic alkalies participate. These compounds have been for the most part, simple compounds of carbon, hydrogen and oxygen of typical classes of carbon compounds. They are better adaptable to determine reaction mechanism and are generally more stable at the elevated temperatures at which the reactions have been conducted.

The hypothesis advanced for the behavior of caustic alkalies when in a fused and anhydrous condition at elevated temperatures assumes the acidic dissociation of the alkali

$$MOH \longrightarrow MO^- + H^+ \qquad (I)$$

where M = Na or K

Here a positive hydrogen atom is split off and this in turn reacts presumably, so to speak, with the negative hydrogen or methyl groups of the organic compound providing the latter are in union with a carbon atom which is in turn united to an oxygen atom, to form gaseous hydrogen or methane.

Two general type reactions have been postulated for these changes:

$$R(H)_n + nMOH \longrightarrow R(OM)_n + nH_2 \qquad (II)$$

$$R(CH_3)_n + nMOH \longrightarrow R(OM)_n + nCH_4 \qquad (III)$$

where M = Na or K.

The purposes of the present research are:

(1) To extend this investigation to the interaction of oxalic acid, its sodium and its methyl and ethyl esters, and also, in this study, the behavior of ethyl formate, ethyl acetate, ethyl carbonate, ethyl ortho-formate and ethyl lactate were likewise examined.

(2) To investigate from the point of view of the above type reactions, the amounts of products formed and thereby to establish stoichiometric ratios between the amounts of the reactants and the amounts of products.

(3) To propose an additional mechanism for the reactions which occur in conformity with the type equations, aiming to determine specifically the behavior of the ethyl group as

contrasted with the methyl group when united with the carbonyl group in organic compounds.

II. HISTORICAL AND THEORETICAL

Previous to the inauguration of the present program of research by Fry [1,2,3,4,5,6] and his coworkers, comparatively few references in the literature include any data relative to the mechanism of reactions of organic compounds with fused anhydrous caustic alkalies. The majority of the experiments investigated placed emphasis merely upon the qualitative significance of the reactions.

The earliest work involving reactions of carbon compounds and caustic alkalies was carried out by Dumas and Stas (1840) [7] who heated a number of organic compounds with potash lime, and anhydrous baryta in glass tubes. The gaseous products were in the main hydrogen and ethylene; while the residues contained formates, oxalates, acetates and carbonates.

Peligot [8] in the same year (1840) reported the decomposition of potassium formate with excess alkali and obtained hydrogen and oxalate, which latter in turn yielded hydrogen and carbonate.

Dumas and Stas [7] maintained that "organic compounds under the influence of alkali take over the oxygen from the water that is present and are oxidized with the liberation of hydrogen which comes jointly from the water and the carbon compound."

Similar work along these lines was carried out by Pelouze and Millon [9] who studied the varying effects of anhydrous and hydrated baryta on organic compounds heated to

high temperatures. They, too, concluded that the mechanism of such reactions must be interpreted as involving the elements of water. They studied a group of reactions and observed the gaseous compounds to consist of either hydrogen, methane or carbon monoxide, the residues containing barium carbonate. They then formulated a generalization that "anhydrous baryta brings out of organic compounds all the carbonic acid their composition permits them to furnish; hydrated baryta carries destruction further and tends to burn or cauterize all the carbon while the hydrogen which is provided by the substances unites with that produced by the decomposition of water and is liberated." A text by Persoz (10) cited by Millon and Pelonze states that all organic substances are decomposed with a great excess of hydrate of potash to give hydrogen.

Buisine in 1903 (11) in studying the reaction of glycerol with excess caustic potash showed that in the preliminary oxidation potassium oxalate and potassium formate were formed which in turn reacted with the alkali to form carbonates and hydrogen. He showed that conversion of the oxalate to carbonate took place above 280°C as follows

$$K_2C_2O_4 + 2KOH \longrightarrow 2K_2CO_3 + H_2,$$

which reaction is similar to that used in the present investigation of oxalic acid derivatives.

Some investigations wherein an attempt was made to explain the mechanisms of reactions of organic compounds with caustic alkalies were those of Hell (12) and Nef (13). The

former carried out reactions of alcohols with caustic alkalies in an attempt to determine molecular weights of the former on the basis of the hydrogen evolved: $R\text{-}CH_2OH + NaOH \rightarrow R.CO_2Na + H_2$.

With higher alcohols he was not able however to obtain quantitative yields of hydrogen, and with lower alcohols he stated that secondary reactions involve gaseous products which interfere with the above reaction; hence his method is not satisfactory for molecular weight determinations. However he was able to distinguish alcohols qualitatively on the basis of this reaction.

Nef (13) carried out the reaction of a number of alcohols with potash lime or soda lime at different temperatures ranging between 170°C-450°C. He obtained hydrogen and salts of organic acids in most cases and in no case were olefines noted.

He employed his results to substantiate his theory of methylene dissociation of aliphatic alcohols

$$CH_3CH\begin{matrix}H\\OK\end{matrix} \longrightarrow CH_3CH< + KOH$$

$$CH_3CH< + 2KOH \longrightarrow CH_3CH(OK)_2 + 2H_2$$

$$CH_3CH(OK)_2 \longrightarrow \begin{matrix}CH_3\\KO\end{matrix}\!\!>C = + KOH + H_2$$

$$CH_3-C\begin{matrix}=\\OK\end{matrix} + HOK \longrightarrow \begin{matrix}CH_3\\OK\end{matrix}\!\!>C(OK)_2 + H_2$$

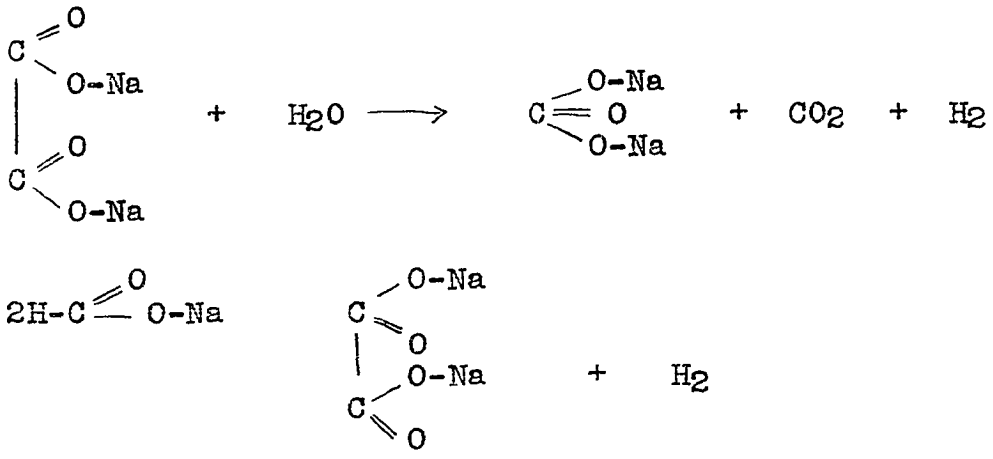
Boswell and Dickson (14) carried out reactions between caustic soda and a number of organic and inorganic compounds such as sodium oxalate, sodium formate, phenol, sulfonic acids, carbon monoxide, etc. They found complete oxidation of carbon

monoxide to alkali carbonate with liberation of one mole of hydrogen at a temperature of 410°C. They then worked with sodium formate and found that by reacting 0.157 grams of sodium formate with 0.352 grams of sodium hydroxide they were able to obtain results as follows: Hydrogen produced 47.9 cc. carbon dioxide produced 50.2 cc; carbon monoxide produced 0.3 cc. and oxygen used up 0.1 cc. No oxalates were found in the solution. The reaction was carried out at 275°C.

They then extended their investigation to sodium oxalate and in this case reacted 0.1982 grams of the oxalate with 0.52 grams of hydroxide. The results were: hydrogen produced 57.9 cc; carbon dioxide produced 63.2 cc; carbon monoxide produced 0.1 cc. and there was no oxygen used up. The solution remaining required permanganate corresponding to 0.0025 grams of oxalate. The temperature of the reaction was 290°C. In addition data was included showing the behavior of sodium formate upon thermal decomposition.

They reached the conclusion that the mechanism of the oxidation of formic acid to carbonic acid, the oxidation of oxalic acid to carbonic acid, and the conversion of formic acid to oxalic acid might be explained by involving the elements of water, the oxygen atom attaching itself to the carbon and hydrogen then is liberated. This then accounts for the liberation of hydrogen and the formation of carbonate. All oxidations are catalyzed by sodium hydroxide. Their reactions are: $CO + H_2O \longrightarrow CO_2 + H_2$

$$H\text{-}C\overset{O}{\leqslant} O\text{-}Na + H_2O \longrightarrow C\begin{matrix} \diagup OH \\ = O \\ \diagdown O\text{-}Na \end{matrix} + H_2$$



Numerous other reference of work done by Lewy, Löwig, Brodie, Gerhardt, Erlenmeyer, Merz, etc. have been reviewed in previous theses (2,3) and have no direct bearing upon the present investigation.

The work of Fry (1,5) and his coworkers, consisting in bubbling vapors of pure organic compounds through fused anhydrous caustic alkalies, eliminates the necessity of explaining the reaction mechanism upon the basis of the elements of water. Hence Fry assumed that the alkalies participate directly in the oxidation and do so through acidic dissociation,

$$MOH \longrightarrow MO^- + H^+ \quad (I) \quad (\text{where } M = Na \text{ or } K)$$

This reacts with carbon compounds according to the type equations

$$R(H)_n + nMOH \longrightarrow R(OM)_n + nH_2 \quad (II)$$

$$R(CH_3)_n + nMOH \longrightarrow R(OM)_n + nCH_4 \quad (III)$$

In all of the reactions of the compounds thus investigated, it was shown that the gaseous products consisted of hydrogen and methane or a mixture of both, while sodium and

potassium carbonates were the only carbon compounds remaining in the reaction residues.

The following table summarizes the reactions of the compounds previously investigated in this laboratory, the average percentage yield of products obtained based upon the theoretical requirements and the temperature at which the reactions were found to proceed most favorably. In several of the compounds investigated two simultaneous reactions (A and B) were found to take place. In (A) complete oxidation to carbonate with the liberation of hydrogen was effected, while in (B) part of the carbon appeared in the form of methane.

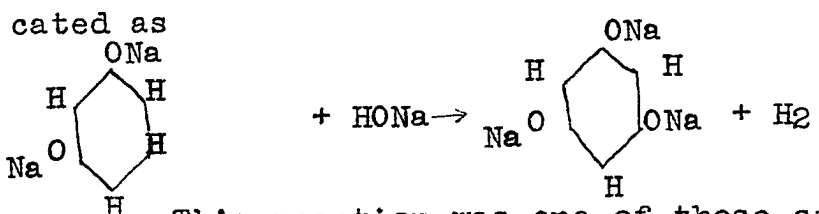
Table A

Summary of Reactions Previously Confirmed

Eq.No.	Equation for Reaction	Temperature	Per cent extent of theory
	Alcohols		
1	$CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + H_2$	450	98
2	$CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + CH_4 + H_2$	530	88
3	$(CH_3)_2CHOH + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4 + H_2$	500	96
4	$(CH_3)_3COH + 2NaOH \longrightarrow Na_2CO_3 + 3CH_4$	510	87
	Aldehydes and Ketones		
5	$CH_2O + 2NaOH \longrightarrow Na_2CO_3 + 2H_2$	325	89
6	$CH_3CHO + 2NaOH \longrightarrow Na_2CO_3 + CH_4 + H_2$	300	94
7	$(CH_3)_2CO + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$	350	91

	Acids		
8	$HCOONa + NaOH \longrightarrow Na_2CO_3 + H_2$	325	98
9	$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4$	300	88
10	$CH_3CHOHCOONa + 3NaOH \longrightarrow 2Na_2CO_3 + CH_4 + 2H_2$	450	88
11	$CH_2OHCOONa + 3NaOH \longrightarrow 2Na_2CO_3 + 3H_2$	550	97
	Esters		
12	$HCOOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2$	350	98
13	$CH_3COOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + CH_4 + 3H_2$	350	88
	Polyhydroxy Compounds		
14	$C_2H_4(OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2$	350	87
15 A.	$C_3H_5(OH)_3 + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2$	450	21
15 B.	$C_3H_5(OH)_3 + 4NaOH \longrightarrow 2Na_2CO_3 + CH_4 + 3H_2$	450	78
16 A.	$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2$	450	10
16 B.	$C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2$	450	90
17 A.	$(C_6H_{10}O_5 + H_2O) + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2$	550	95
17 B.	$(C_6H_{10}O_5 + H_2O) + 8NaOH \longrightarrow 4NA_2CO_3 + 2H_2O + 4H_2 + 2CH_4$	550	5

A key to the mechanism of the above reactions was found in the well known conversion of resorcinol into phloroglucinol upon fusion with sodium hydroxide. This is accompanied by a vigorous evolution of hydrogen, and the reaction may be indicated as



This reaction was one of those studied by Boswell and Dickson (14) who claimed that "the reaction does not give off

hydrogen until the compound is first heated with access to atmospheric oxygen which it absorbs and is thus presumably been oxidized to some compound which does take part in the reaction." Schulze (3,17) repeated this reaction in an atmosphere of hydrogen and obtained results substantiating the above reaction to the extent of 90 per cent and this invalidated the conclusions of Boswell and Dickson.

The above reaction is a simple illustration of the general type equation

$$R(H)_n + nHONa \longrightarrow R(ONa)_n + nH_2$$

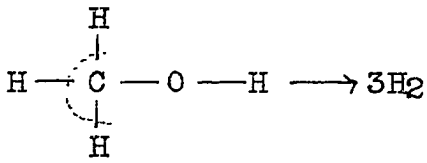
which was assumed by Fry to indicate the amphoteric behavior of sodium hydroxide.

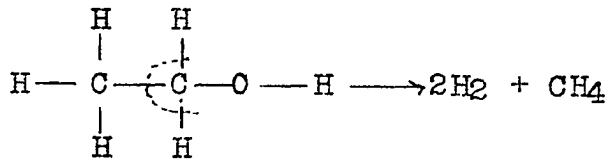
Now all of the equations in the Table A above (1-13) may be derived in the same manner by applying consecutively one or both of the similar type equations (II and III) to the constituent atoms of the molecule of the compounds investigated. The summation of the intermediate equations gives the completed equation.

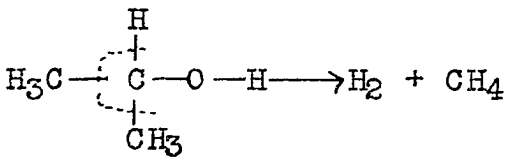
A further insight into the mechanism of reactions (1-13) may be gained by studying the structural formulae of each of these thirteen compounds and noting the number of hydrogen or methyl or both hydrogen and methyl radicals which combine with hydrogen atoms of the alkali hydroxide to yield hydrogen or methane or both hydrogen and methane. These are tabulated as follows:

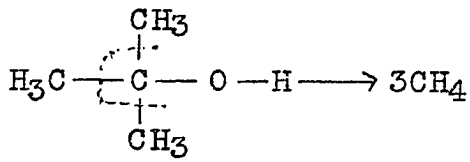
Structural Formulae Indicating Mechanism of Reactions

Alcohols - primary, secondary and tertiary

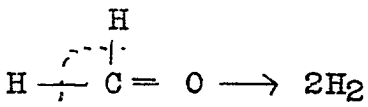


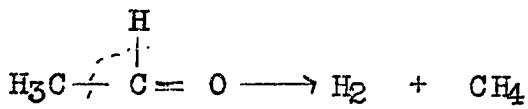


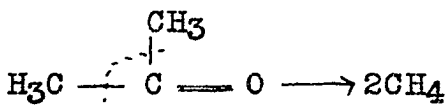




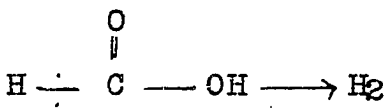
Aldehydes and Acetone

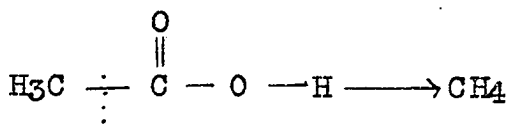


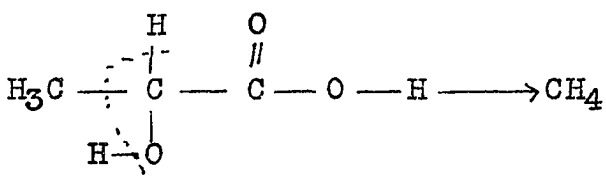


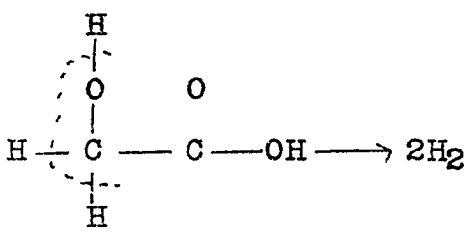


Acids

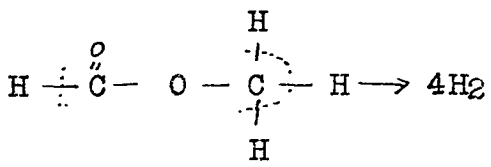


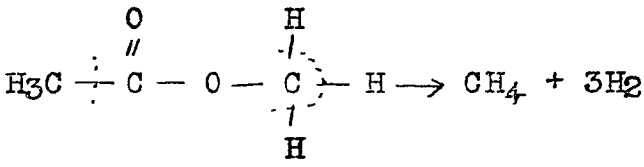






Esters





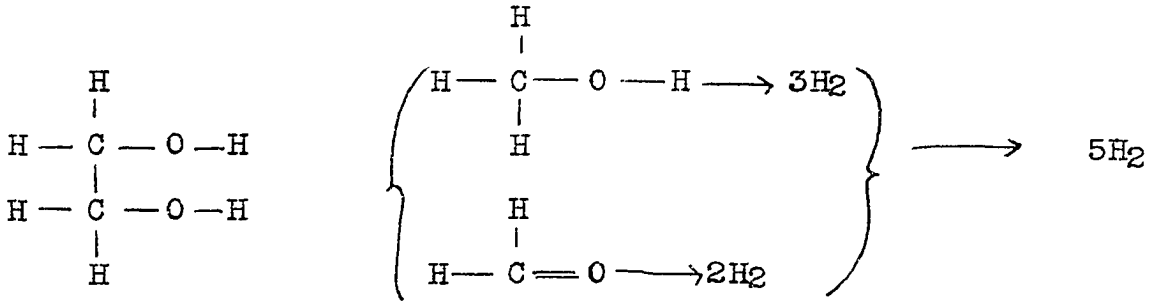
From the above notation a second rule relative to the mechanism of reactions has been proposed by Fry, namely, that every hydrogen atom and every methyl radical in union with a carbon atom which carbon atom is in turn united to an oxygen atom, yields, respectively a molecule of hydrogen a molecule of methane when the compound reacts with fused caustic alkali.

This specific rule is not directly applicable in the case of glycol, glycerol, dextrose, levulose and cellulose, which exceptions do not, however, invalidate the rule as will be shortly explained. In the case of Rochelle salt (sodium potassium tartrate) the behavior with fused caustic alkalies is not in conformity with the specific rule and no reconciliation has so far been developed. This is the only exception which has been encountered.

In the case of the five compounds above, the specific rule was applied by first assuming that these more complex molecules on interaction are first resolved into simpler molecules and the latter in turn react in complete conformity with the rule and give yields of products demanded by the theory as expressed in the derived summation equations.

Thus in the case of glycol it was assumed that one molecule of glycol behaved as if it were equivalent to one molecule of methyl alcohol and one molecule of formaldehyde.

Now it has been shown in separately conducted experiments with these compounds that the former yields $3H_2$ and the latter $2H_2$. The total yield $5H_2$ then indicates that glycol reacts according to the scheme



The complete reactions involved are

$$C_2H_4(OH)_2 \longrightarrow CH_3OH + CH_2O \qquad (a)$$

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

$$CH_2O + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 \qquad (c)$$

$$\Sigma\ (a)(b)(c) \quad C_2H_4(OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (14)$$

The reaction of glycerol with fused caustic alkalies was explained upon the same basis. It was assumed that one molecule of glycerol upon reaction was equivalent to one molecule of methyl alcohol plus two molecules of formaldehyde.

The following equations explain the final reaction

$$C_3H_5(OH)_3 \longrightarrow CH_3OH + 2CH_2O \qquad (a)$$

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

$$2CH_2O + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2 \qquad (c)$$

$$\Sigma\ (a)(b)(c) \quad C_3H_5(OH)_3 + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \qquad (15A)$$

The mechanism of the reactions found to occur with dextrose, levulose and cellulose were found to be quite in

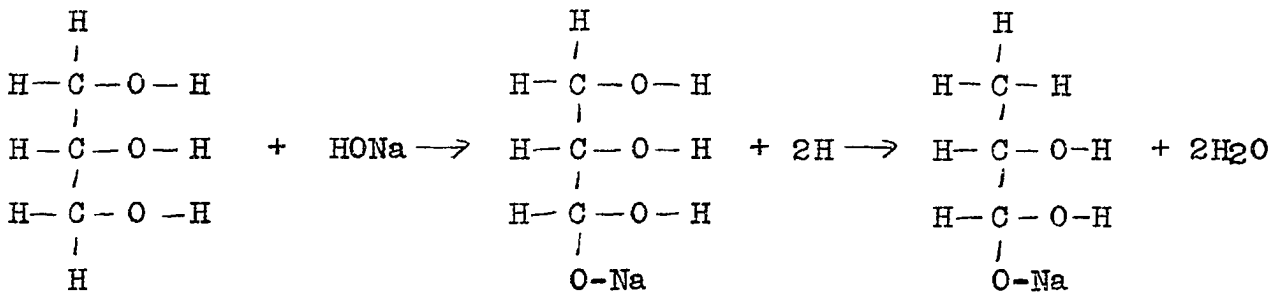
conformity with the principles and reaction mechanism schemes illustrated above.

In the reactions of glycerol, dextrose, levulose and cellulose two independent reactions were represented. In the case of equations 15B, 16B and 17B of Table I, methane was liberated and the specific rule governing the behavior of the carbon compounds with alkalies could not be applied directly.

As the complex molecules of glycerol, dextrose, levulose and cellulose contain no methyl radicals, it was necessary to postulate that they undergo an intra-molecular oxidation-reduction reaction which leads to the formation of methyl radicals. Alkalies in many cases induce intra-molecular oxidation-reduction changes. The type equation $RH + HONa \longrightarrow RONa + 2H$ thus postulates the formation of hydrogen which is not liberated as gaseous hydrogen but effects the reduction of a $-CH_2OH$ group at another carbon atom of the molecule to form a $-CH_3$ radical

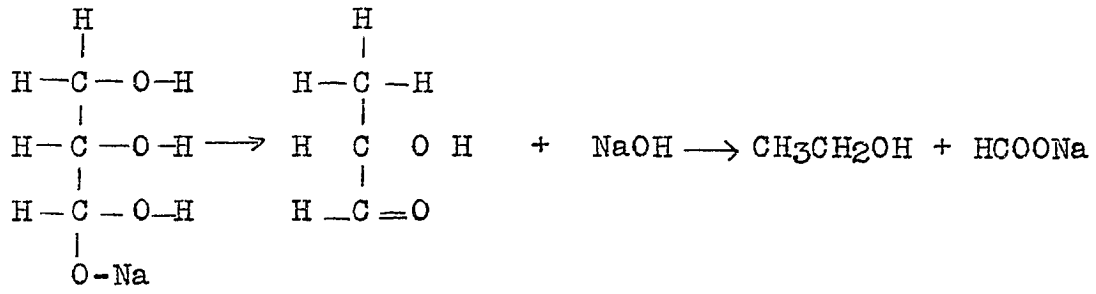
$$R{-}CH_2OH + 2H \longrightarrow R{-}CH_3 + H_2O$$

The scheme of the reaction as applied to glycerol is as follows:



The resultant molecule is assumed to lose a molecule of sodium hydroxide (or it is hydrolyzed to yield sodium hydroxide and α-hydroxy ortho propionic aldehyde) forming α-hydroxy

propionic aldehyde which reacts with the alkali to yield one molecule of ethyl alcohol plus one molecule of sodium formate



and the complete proposed intermediate reaction leads to the equation

$$C_3H_5(OH)_3 + NaOH \longrightarrow CH_3CH_2OH + HCOONa$$

Hence the completed reaction of glycerol with caustic alkalies to yield both hydrogen and methane may be postulated as follows

$$C_3H_5(OH)_3 \longrightarrow CH_3CH_2OH + HCOOH \qquad (a)$$

$$CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4 \qquad (b)$$

$$HCOOH + 2NaOH \longrightarrow Na_2CO_3 + H_2O + H_2 \qquad (c)$$

$$(a)(b)(c)\quad C_3H_5(OH)_3 + 4NaOH \longrightarrow 2Na_2CO_3 + H_2O + 3H_2 + CH_4 \qquad (15B)$$

This mechanism for intra-molecular oxidation-reduction reactions may be extended to the molecules of dextrose, levulose and cellulose in which cases it is assumed the hexose molecule reacts as being equivalent to two molecules of lactic acid. This fact is in harmony with experimental data as alkalies convert certain hexoses and cellulose into lactic acid.

The reaction mechanism for these poly hydroxy compounds is thus shown

$$C_6H_{12}O_6 \text{ or } (C_6H_{10}O_5 + H_2O) \longrightarrow 2CH_3CHOHCOOH \qquad (a)$$

$$2CH_3CHOHCOOH + 2NaOH \longrightarrow 2CH_3CHOHCOONa + 2H_2O \qquad (b)$$

$$2CH_3CHOHCOONa + 6NaOH \longrightarrow 4Na_2CO_3 + 4H_2 + 2CH_4 \qquad (c)$$

$$\Sigma\,(a)(b)(c) \quad C_6H_{12}O_6 \text{ or } (C_6H_{10}O_5 + H_2O) + 8NaOH \longrightarrow$$

$$4Na_2CO_3 + 2H_2O + 4H_2 + 2CH_4 \qquad \begin{matrix}(16B)\\(17B)\end{matrix}$$

The reaction of lactic acid and sodium lactate as indicated above has been shown to conform experimentally to the theoretical postulate.

The behavior of sodium potassium tartrate with fused anhydrous caustic alkalies is analogous to the behavior of poly hydroxy compounds in so far as methane is evolved while the organic molecule itself contains no methyl group. This indicates an intra-molecular oxidation-reduction reaction as occurring which in turn serves to produce an intermediate compound possessing a methyl group. However to date no theoretical postulate has yielded equations in conformity with the experimentally determined amounts of products obtained.

This survey of previous work conducted in this laboratory fully illustrates the principle and the reaction mechanism schemes developed in the course of the present investigation.

III. APPARATUS AND PROCEDURE

A. Apparatus

To carry out the reactions between fused anhydrous caustic alkalies and carbon compounds a special apparatus was used which could be varied depending upon the nature of the organic compound under investigation. The entire apparatus is shown on the accompanying photograph.

The description of the general apparatus has already been described (3,4,5) and will not be repeated here. An improvement over the previously described method was made by collecting any gas evolved which contained methane in gasometers initially filled with saturated sodium chloride solution in which the methane is specifically much less soluble. This makes for the securing of more complete yields of the gas. In cases where hydrogen alone was evolved, the confining liquid was simply pure water: and the gas analysis was carried out immediately after the cessation of the reaction so as to minimize the solubility effects.

Several types of heating bath were used. For the first few determinations, a graphite crucible was employed which had a diameter of 10 centimeters and a depth of 15 centimeters, filled with solder. The iron reaction tube was inserted to a depth of 8 centimeters. The fusion temperature of the solder used in all the reactions investigated was around 160°C. The heating in this case was carried out by use of a Fischer burner and the entire device was properly shielded from drafts

by means of a wall of bricks. This arrangement enabled a smoother and more uniform heating of the reaction mixture to be effected than was formerly the case, but possessed as a disadvantage the fact that the graphite not being essentially a good conductor retarded the flow of heat into the solder and hence unduly lengthened the time required to complete a given reaction, and moreover usually precluded a high reaction temperature being attained.

To obviate these difficulties a second type of heating device was developed. This consisted of an iron cylindrical crucible having a diameter of 11 centimeters and a heigth of 23 centimeters, supported on a specially constructed ring stand 30 centimeters high, filled with solder to a depth of 12 centimeters, which thus enabled a larger volume of the reaction tube to be heated. As before the Fischer burner was employed for heating, and a wall of bricks was built around the entire apparatus to protect it from draft and to prevent undue radiation.

For the investigations made during the year 1930-31 a still more compact and more efficient heating device was used. This consisted of an iron crucible similar to the above, filled with solder to a heigth of 12 centimeters. The heating was effected by use of a specially constructed gas burner ring 9 centimeters in diameter, located below the solder bath and attached to the gas lead. It contained about thirty gas ports, which enabled a flame of high temperature being attained. The crucible was surrounded on side and on top by a coating of

asbestos 3 centimeters thick to prevent undue radiation. The whole was supported by three attached legs 9 centimeters high. This apparatus eliminated the use of the Fischer burner and the wall of bricks. It has proven to be the most satisfactory apparatus for heating employed so far in this series of researches.

The temperature of the bath was measured with a chrome aluminal thermocouple connected to a millivoltmeter. The temperature range employed in the fusion reactions was 450°-500°C.

B. Preparation of the Fused Alkali

Before employing alkalies in these reactions a preliminary fusion is necessary to drive off water that is present and to saturate the alkali with oxides of iron so that no further reaction between the iron reaction tube and the alkali is possible.

For this purpose one or two pounds of Merck's purest alkali was placed in a cast iron crucible, having a diameter of 15 centimeters and a depth of 15 centimeters and this in turn placed in a Monarch pot furnace.

The alkali was heated to a temperature of 800°C and kept there until all of the water was driven off which was effected when quiet liquid fusion was noted. After about five additional minutes of heating the molten alkali was poured upon a cold iron plate where it rapidly solidified. It was then broken up into small pieces and bottled. Ten pounds each of

sodium and potassium hydroxide were thus treated at the beginning of each year's work.

The carbon dioxide content of each of the fused caustic alkalies must be quantitatively determined in view of the fact that alkali carbonates are formed in the reaction chamber during the course of the oxidation, thereby necessitating a correction for the amount of carbon dioxide in the alkali to be made.

To this end, ten gram samples of the alkali were accurately weighed and decomposed with excess sulfuric acid. The carbon dioxide thus obtained is weighed directly, according to the method described below.

The results obtained are as follows:

Alkalies used during 1929 - 1930

Sodium hydroxide

Determination	I	II	III	Average
% CO_2	2.75	2.72	2.73	2.73

Potassium hydroxide

Determination	I	II	III	Average
% CO_2	1.62	1.66	1.70	1.66

Alkalies used during 1930 - 1931

Sodium hydroxide

Determination	I	II	III	Average
% CO_2	1.22	1.20	1.16	1.19

Potassium hydroxide

Determination	I	II	III	
% CO_2	0.74	0.72	0.71	0.72

Upon the basis of these analyses, calculations for the content of carbonate as carbon dioxide in the sodium hydroxide-potassium hydroxide mixture were made.

C. Method of Procedure

The alkali charge used in all of the experiments of this research was similar to that used in the previous investigations, namely an eutectic mixture of caustic soda and potash consisting of 55.3 grams of sodium hydroxide and 51.1 grams of potassium hydroxide. This mixture possesses a melting point of about 185°C. The alkalies were pulverized in a mortar before use. This expedited their accurate weighing, facilitated ready mixing in the reaction tube, and in the case of the reaction of solid organic compounds enabled the reaction to proceed more uniformly toward completion.

Where liquid organic compounds were investigated (other than ethyl formate, where the alternate method of procedure is described under the appropriate heading in the following section) the procedure consisted of pipetting a measured amount of the liquid sample into the Walther dropping funnel. The pressure equalizing tube was next sealed to the funnel, and the leg of the dropping funnel was securely inserted through a rubber stopper so as to extend through the upper end of the inner tube of the reaction chamber.

The bath was then heated to between 450°C and 500°C and then the liquid was slowly introduced, a few drops at a time, sufficient time being allotted between drops to enable

the bulk of the gas to be slowly collected in the gasometer. After all of the reacting liquid compound was added, heating was continued until evolution of the gas had ceased.

In the runs with solid organic compounds (other than dimethyl oxalate where the special method of procedure employed is described under the appropriate heading in the next section) the iron tube containing the alkali was first placed into the bath and a weighed quantity of the sample was added to the powdered alkali. This mixture was then stirred to obtain adequate distribution of sample and alkali charge. The tube was then closed with a screw cap and sealed with a glycerine-litharge paste. The heating was conducted very slowly since the reaction at the start was quite vigorous.

After the reaction was completed, the solid residue in the reaction tube contained the carbon dioxide yield present as alkali carbonates. After cooling the reaction tube to room temperature, the mixture of alkali hydroxides and carbonates was dissolved out in hot water. The solution was most readily effected by first removing the inner tube from the reaction mixture when it was still molten. The inner tube upon cooling was immersed in a beaker of hot water, and the alkali still clinging to the lower section of it allowed to dissolve.

To the residue in the reaction tube, portions of about 50 cc. of hot water were added and the whole was then shaken vigorously for several minutes. Three or four treatments were sufficient to dissolve completely the entire residue. The combined solutions thus obtained were placed in a three liter

bottle and allowed to stand for six or eight hours, that is until all of the suspended material had settled. It was then filtered by use of a special apparatus which excluded absorption of carbon dioxide from the air. This filtrate was then diluted to two liters and an aliquot portion, namely 25cc., was used for each carbon dioxide determination.

D. Analysis of the Reaction Products

The estimation of the carbon dioxide was accomplished by use of a Knorr (21,22) Apparatus. The method consists in adding an excess of sulfuric acid to the sample in a closed system consisting of a decomposition flask, a vertical condenser, two U-tubes, one of which contains glass beads saturated with concentrated sulfuric acid in which is dissolved silver sulfate. The second U-tube was filled with anhydrous calcium chloride. The remainder of the train consisted of the ascarite column, wherein the carbon dioxide is absorbed, a calcium chloride tube and a gas washing bottle containing about 3 cc. of concentrated sulfuric acid which serves as a bubble counter. To this is connected a side necked suction flask which in turn is connected to a water pump. The flask serves as a water trap.

The gas from the decomposition flask is drawn through the condenser by means of a slow stream of air free from carbon dioxide. It then passes through the sulfuric acid U-tube where it loses part of its moisture. Any halogen acid which may be present is here removed by the silver sulfate.

The gas then passes through the calcium chloride U-tube where any remaining water vapor that may be present is removed. From here the gas passes into the ascarite tower where the carbon dioxide is absorbed. To the upper end of the ascarite tower is attached the calcium chloride tube which serves as a guard. The ascarite tower is weighed before and after each run, the gain in weight representing the carbon dioxide in the sample.

All the connections in the train were pealed with the de-Kohtinsky cement to make them gas tight.

The analysis of the gas was carried out according to standard methods.(23,24) The gaseous products of the reactions consisted of hydrogen and methane only. This was usually accompanied by a small percentage of inert air present in the apparatus at the start.

In each analysis a sample of approximately 10 cc. was drawn off and this was exploded with excess oxygen. The contraction in volume was noted and the carbon dioxide resulting was absorbed in concentrated potassium hydroxide. From these data the amounts of hydrogen and methane were calculated according to the well known equations:

$$\text{vol. of } CO_2 = \text{vol. } CH_4$$

$$\text{vol. of } H_2 = 2/3\ (\text{contraction} - 2 \times \text{vol. } CO_2).$$

IV. EXPERIMENTAL

Part 1. Compounds not Containing the Ethyl Radical

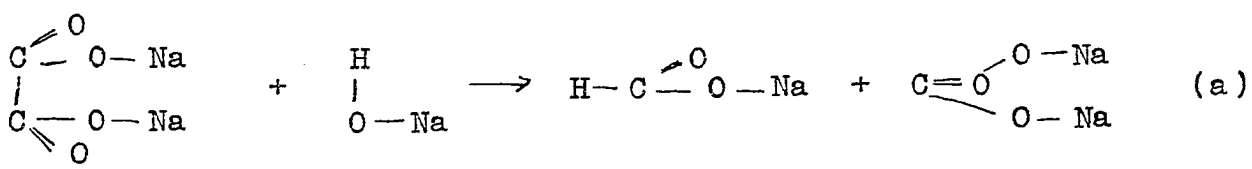
A. Sodium Oxalate

Our attention was first turned toward sodium oxalate since this compound is a derivative of the simplest dibasic acid, in which series no previous work in regard to the behavior of these compounds with fused anhydrous caustic alkalies has so far been attempted.

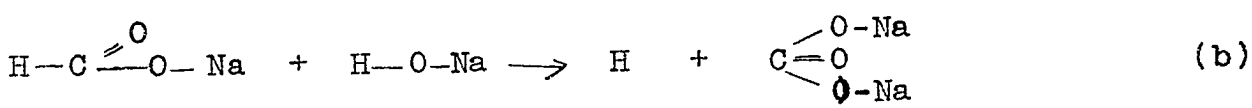
Boswell and Dickson [14] reacted samples of sodium formate and sodium oxalate with caustic soda under conditions somewhat different from those outlined above. They determined as end products of the reaction hydrogen and carbon dioxide which might be expected; however they attempted to explain the mechanism of their reaction by involving the ions of water. Moreover no specific equation governing the reaction is proposed by them.

We then attempted to study the reaction of pure anhydrous sodium oxalate with fused anhydrous caustic alkalies to correlate the amounts of products obtained with those demanded by the general type equations (I) and (II).

The reaction may be assumed to proceed in either of two ways, viz:



(a)



(b)

$$\Sigma(a)(b) \quad \begin{matrix} C(=O)-O-Na \\ | \\ C(=O)-O-Na \end{matrix} + 2HONa \longrightarrow H_2 + 2Na_2CO_3 \qquad (IV)$$

The second interpretation is based upon the well known fact that sodium oxalate under the influence of heat decomposes into carbon moncxide and sodium carbonate. The reaction may then be pictured as

$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} \longrightarrow Na_2CO_3 + CO \qquad (a')$$

$$CO + 2NaOH \longrightarrow Na_2CO_3 + H_2 \qquad (b')$$

Reaction (b') has been studied in the light of the present program of research by Fry and Schulze.

The summation of the two reactions gives the equation

$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2NaOH \longrightarrow 2Na_2CO_3 + H_2 \qquad (IV')$$

which is identical of course to reaction IV above. This again is an example of the general type equation

$$R(OH)_n + nMOH \longrightarrow R(OM)_n + nH_2 \qquad (II)$$

It is particularly noteworthy that the sodium oxalate contains no hydrogen and since the alkali is water free the appearance of hydrogen must necessitate the acidic dissociation of the alkali. No other explanation is apparent.

The purest Merck's sodium oxalate namely that specified for permanganate standardization was used. Exactly one third of a mole or 44.70 grams was employed in each run. This was intimately mixed with the alkali charge and placed in the reaction tube which was in turn inserted into the bath.

The temperature of the bath was slowly raised to 400°C where it was kept stationary until the reaction was complete. A vigorous evolution of gas occurred at about 250°C. About six hours were required to complete the reaction which was no doubt due to the large amount of sample used. The gas evolved consisted simply of hydrogen and a little air originally present in the apparatus.

The experimental data are included in Table II.

Table II

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters	Per cent yield
I	7.23	7.47	96.8
II	7.35	7.47	98.4

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	28.93	29.33	98.63
II	29.17	29.33	99.45

Unreacted Sodium Oxalate at end of Reaction

Run	I	II
Amount	0.192 gms.	0.096 gms.

The amounts of undecomposed sodium oxalate remaining in the fused residue at the end of the run is negligible in comparison with the original sample.

The results indicate that the general type equations

and mechanism apply to the behavior of sodium oxalate with fused anhydrous caustic alkalies in conformity with equation IV. The mechanism of Boswell and Dickson, while applicable under their experimental conditions, certainly does not apply here.

B. Oxalic Acid

It was next considered advisable to investigate the reaction of pure oxalic acid of formula $\begin{matrix}COOH\\|\\COOH\end{matrix}.2H_2O$ with anhydrous caustic alkalies.

Williams [5] while working with several organic acids found that a greater yield of reaction products demanded by the type equation were obtained if the sodium salts of the acid were employed. This difference was attributed to the fact that when the pure acid was employed, one molecule of water was liberated by preliminary neutralization which in turn tended to repress the acidic dissociation of the alkali and favor basic dissociation which would tend to limit the extent of the reaction.

The author found that in the case of lactic acid and sodium lactate, the amounts of the reaction products obtained are practically similar and the above hypothesis is not necessarily pertinent here.

To further investigate the reaction of organic acids from this point of view and to determine whether water of crystallization present in any way influenced the reaction

mechanism it was logical to investigate the reaction of oxalic acid next.

The proposed reaction which may be postulated according to principles identical with those used above for sodium oxalate is

$$\begin{matrix}COOH \\ | \\ COOH\end{matrix} .2H_2O + 4ROH \longrightarrow 2R_2CO_3 + H_2 + 4H_2O \qquad (V)$$

where R = Na or K.

The purest oxalic acid obtainable was employed, this being analyzed for purity by permanganate titration.

For the experimental runs, one third of a mole or 42.02 grams of oxalic acid containing two molecules of water of crystallization was employed in each run. The sample was mixed intimately with the alkali in a manner similar to that described above.

The reaction evolved considerable gas at a temperature around 200°C. The final temperature to which the reaction mixture was heated was 400°C and the time required for the reaction to be completed varied from six to eight hours.

The experimental data follow in Table II

Table II

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters	Per cent yield
I	7.35	7.47	98.4
II	7.40	7.47	99.1

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	28.55	29.33	97.34
II	29.01	29.33	98.91

Unreacted Oxalic Acid

Run	I	II
Amount	0.10	0.09

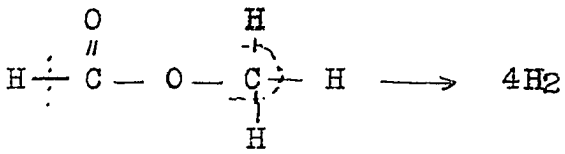
The unreacted oxalic acid in the reaction residue is here also negligible in comparison to the amount of sample used.

Hence we may conclude that the oxidation of oxalic acid containing two molecules of water of crystallization when reacted with fused anhydrous caustic alkalies proceeds according to the type equation (V) expressed above. The per cent yields of the products are practically equal to those obtained in the case of sodium oxalate and we may conclude that the proposed hypothesis of Williams regarding the behavior of organic acids and their salts is not generally applicable to these cases.

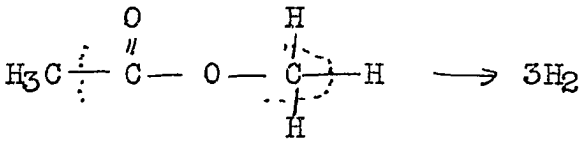
C. Di Methyl Oxalate

The investigation from this point on centered about the reactions of the esters of organic acids with fused anhydrous caustic alkalies. The behavior of the methyl esters of formic and acetic acid with alkalies was investigated by Fry and Otto [4,18]. The results they obtained coincided with those demanded by the type equation.

The general type reactions of esters with fused anhydrous caustic alkalies was proposed by Fry as

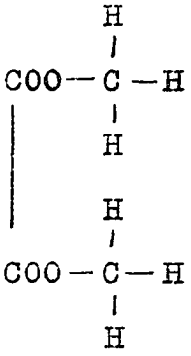


$$\longrightarrow 4H_2$$



$$\longrightarrow 3H_2 + CH_4$$

The reaction of di-methyl oxalate may be postulated upon these basic principles. We assume first preliminary hydrolysis of the ester by the alkali and then the subsequent oxidation of the products so formed.



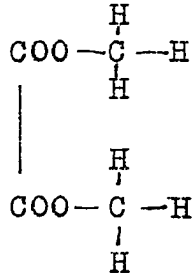
$$+ \quad 2ROH \longrightarrow \begin{matrix} COOR \\ | \\ COOR \end{matrix} + 2CH_3OH \qquad (a)$$

$$\begin{matrix} COOR \\ | \\ COOR \end{matrix} + 2ROH \longrightarrow 2R_2CO_3 + H_2 \qquad (b)$$

$$2CH_3OH + 4ROH \longrightarrow 2R_2CO_3 + 6H_2 \qquad (c)$$

The summation of these partial equations leads to

$\Sigma(a)(b)(c)$



$$+ \quad 8ROH \longrightarrow 4R_2CO_3 + 7H_2 \qquad (VI)$$

where R = Na or K.

Equation (c) has been verified experimentally by Fry and Otto (4,18) and equation (b) has been verified above.

For the experimental determinations the purest Eastman methyl oxalate having a melting point of 52°C was used.

The reaction of methyl oxalate with caustic alkalies at elevated temperatures presented several unusual experimental difficulties. This substance possesses a melting point of around 52°C and a boiling point of 163°C, more than twenty degrees below that of the minimum temperature at which the alkalies fuse.

On a preliminary investigation an attempt was made to react it after the same manner that solid organic compounds are handled. One fourteenth of a mole or 8.43 grams of the compound was weighed out, mixed with the alkali and the reaction tube sealed with a screw cap. The reaction was then carried out in the customary manner, but the gas yield being far less than the theory demanded indicated that volatilization of the organic compound had occurred before it had an opportunity to react with the alkali. This method was then abandoned.

A second possibility presented itself, namely to dissolve di-methyl oxalate in a solvent inert to caustic alkali, ether being the only common one available, and introducing the solution into the reaction mixture in the same manner organic liquids are handled.

This did not prove feasible because of the extreme volatility of the ether which in the method used could not be

retained in the dropping funnel. This leakage courted danger.

The method finally used, which proved quite satisfactory, consisted in introducing the organic compound in its liquid form. A weighed amount of the solid ester was introduced into the bulb of the dropping funnel which in turn was attached to the reaction tube. The radiation from the metal bath impinging upon the dropping funnel caused its temperature to rise above the melting point of the ester, hence the latter dropped readily into the alkali as a liquid.

Of the runs made, three showing closest concordance are tabulated below. In two of these, one twenty-eighth of a mole of ester was employed, in the third, one fourteenth of a mole was employed.

The reactions were carried out at a temperature of about 450°C.

The experimental data are included in table III below.

Table III

Hydrogen

Run	Sample gms.	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	4.22	5.20	5.60	92.9
II	4.22	5.23	5.60	93.2
III	8.44	10.3	11.20	91.9

Carbon Dioxide

Run	Sample gms.	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	4.22	5.65	6.29	89.8
II	4.22	5.66	6.29	90.0
III	8.44	12.05	12.57	95.8

Unreacted methyl oxalate at conclusion of the reaction

Run	I	II	III
Amount in gms.	0.011	0.011	0.023

The data in Column 4 shows that the per cent theoretical yield of hydrogen and carbon dioxide, respectively 92%-93% and 89%-96%, being within the limits of experimental error, confirm the occurrence of the postulated reaction represented by equation (VI) which was derived through the summation of the intermediate type reactions assumed in the reaction mechanism scheme.

Part 2. Compounds containing the Ethyl Radical

No previous work upon the reaction of ethyl esters with anhydrous alkalies has been carried out from the point of view of the present investigations. The research from this point on is resolved thus into a study of the ethyl esters of several typical organic acids, with a view to determine whether or not ethane is evolved. If ethane is not evolved but hydrogen and methane are obtained, the study will then be concerned with the mechanism of the reaction which has lead

to these results. In other words, will the ethyl radical be disengaged as ethane or as a mixture of hydrogen and methane, the rational expectation in the light of previous researches by Fry and Otto upon ethyl alcohol?

D. Diethyl Oxalate

Di ethyl oxalate was the next compound to be investigated. The reaction mechanism for its behavior with caustic alkali may be postulated according to the general type equations and also by use of the additional rule suggested by Fry [15] namely "that every hydrogen atom and every methyl radical in union with a carbon atom, which carbon atom is in turn united to an oxygen atom yields respectively a molecule of hydrogen and a molecule of methane when the compound reacts with the fused caustic alkali."

Accordingly, one might expect that the ethyl radical would yield one molecule of methane, two molecules of hydrogen, and one molecule of carbon dioxide as alkali carbonate. From this point of view the assumed decomposition of diethyl oxalate would be in conformity with the following scheme of intermediate reactions.

$$\begin{matrix} O=C-O-CH_2-CH_3 \\ | \\ O=C-O-CH_2-CH_3 \end{matrix} + 2ROH \rightarrow \begin{matrix} O=C-O-R \\ | \\ O=C-O-R \end{matrix} + 2CH_3CH_2OH \qquad (a)$$

$$\begin{matrix} O=C-O-R \\ | \\ O=C-O-R \end{matrix} + 2ROH \longrightarrow 2R_2CO_3 + H_2 \qquad (b)$$

$$2CH_3CH_2OH + 4ROH \longrightarrow 2CH_4 + 4H_2 + 2R_2CO_3 \qquad (c)$$

$$\leq(a)(b)(c)\quad \begin{matrix} O{=}C{-}O{-}CH_2{-}CH_3 \\ | \\ O{=}C{-}O{-}CH_2{-}CH_3 \end{matrix} + 8ROH \rightarrow 2CH_4 + 5H_2 + 4R_2CO_3 \quad (VII)$$

Reaction (c) has been confirmed by Fry, Schulze, and Otto (3,4,17,18).

The purest Eastman ethyl oxalate was used. This was redistilled and the fraction boiling between 182°C and 183°C was used in the determinations. The sample employed in each run was 10 cc. (10.75 grams). This was pipetted into the Walther dropping funnel, and slowly added to the fused alkali at a temperature of 450°C, sufficient time being allowed for as complete a reaction as possible to take place. After the sample was completely added the temperature was raised to 500°C and heating continued until no more gas was evolved. The reaction consumed about eight hours for completion.

The data obtained are tabulated in Table IV.

Table IV

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	7.51	8.05	93.3
II	7.77	8.05	95.3
III	7.53	8.05	93.5

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	2.91	3.22	90.4
II	2.78	3.22	86.3
III	2.85	3.22	88.5

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	9.50	12.95	73.4
II	9.50	12.95	73.4
III	9.26	12.95	71.6

	Run I	Run II	Run III	Theoretical
Volume ratio H_2:CH_4	2.6:1	2.8:1	2.6:1	2.5:1

Unreacted oxalates in the reaction mixture were negligible in quantity while the yields of methane and hydrogen confirm the postulated equation VII. The yield of carbon dioxide is abnormally low. This apparent discrepancy may be readily explained by the presence of free carbon which undoubtedly arose from the decomposition of the intermediately formed alkali oxalate. The oxalates in the reaction mechanism scheme are first resolved into carbonate and formate and the latter have been shown in previous investigations to form free carbon which is always accompanied with a reduced yield of carbonates. In other words when diethyl oxalate interacts with fused caustic alkali, the intermediate reactions (VIIa) and (VIIc), the latter being responsible for the yields of hydrogen and methane, occur to the extent of about 90 per cent of the theoretical, while the reaction represented by (VIIb) suffers secondary changes explained above.

E. Ethyl Formate

This is the simplest ethyl ester of any organic acid and its reaction with caustic alkalies may be expected to be in

conformity with the general type equations. Formic acid, sodium formate, and methyl formate react with alkalies to give products in accordance with those demanded by the theory.

The specific mechanism proposed is as follows

$$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + ROH \longrightarrow HCOOR + CH_3CH_2OH \qquad (a)$$

$$H-COOR + ROH \longrightarrow H_2 + R_2CO_3 \qquad (b)$$

$$CH_3CH_2OH + 2ROH \longrightarrow CH_4 + 2H_2 + R_2CO_3 \qquad (c)$$

$$\therefore (a)(b)(c) - H-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + 4ROH \longrightarrow CH_4 + 3H_2 + 2R_2CO_3 \qquad (VIII)$$

To investigate the reaction, the material used was the redistilled purest Eastman ethyl formate boiling between 52°C and 54°C.

Due to the low boiling point and hence extreme volatility of ethyl formate, the customary method of introducing liquids into the fused alkalies by way of a Walther dropping funnel could not be employed especially so with the considerable radiation evolved from the heating bath.

The apparatus was therefore modified by substituting for the dropping funnel a glass delivery tube bent to an angle of 90°. To the end of this was attached a glass stopcock which in turn was connected to a delivery tube bent downwards through 90° to connect to a 50 cc. round bottom flask. The whole apparatus was then sealed; all the connections being covered with a thin film of Duco cement which proved efficient for insuring gas tight joints. A thick sheet of asbestos was placed between the furnace and the flask to protect the latter from radiation.

The method now consisted in introducing about 8-9 grams of ethyl formate into the flask, closing the stopcock and weighing flask and stopcock accurately. The flask and stopcock were then connected to the delivery tube which led to the reaction tube. The furnace in the meantime was heated up to the desired reaction temperature, about 450°C. The sample was now introduced by gently heating the flask to vaporize the ethyl formate which was distilled directly into the fused alkali. At the conclusion of the reaction, the stopcock was again closed, the flask and stopcock removed from the apparatus and weighed. The loss in weight indicated the amount of sample reacting, and from this the theoretical amounts of methane, hydrogen and carbon dioxide could be calculated.

The results obtained are listed below in table V.

Table V.

Hydrogen

Run	Wt. of sample gms.	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	8.71	6.25	7.90	79.0
II	8.47	6.42	7.68	83.6
III	8.87	6.89	8.04	85.7

Methane

Run	Wt. of sample gms.	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	8.71	2.21	2.63	84.0
II	8.47	2.16	2.56	84.3
III	8.87	2.32	2.68	86.6

Carbon Dioxide

Run	Wt. of sample gms.	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	8.71	8.22	10.36	79.3
II	8.47	7.82	10.07	77.6
III	8.87	8.30	10.55	78.7

	Run I	Run II	Run III	Theoretical
Volume ratio $H_2:CH_4$	2.83:1	2.97:1	2.98:1	3:1

The results are quite comparable, in fact appreciably better than those obtained by Fry and Otto for methyl formate.

Hence we may conclude that methyl formate interacts with the fused alkali according to the summation equation VIII above.

F. Ethyl Acetate

The reaction of the methyl ester of acetic acid with fused anhydrous caustic alkalies has been studied by Fry and Otto, who found that this compound reacts in general with alkali in accordance with the general type equation, although in all cases where acetic acid and its derivatives have been reacted with caustic alkalies, during the present program of

research, a considerable excess of hydrogen over methane and carbon dioxide as demanded by the specific reaction mechanism and the general type equation has always been noted. As yet this discrepancy has not been reconciled with the theory.

The type reaction mechanism for ethyl acetate is as follows:

$$CH_3COOCH_2CH_3 + ROH \longrightarrow CH_3COOR + CH_3CH_2OH \quad (a)$$

$$CH_3COOR + ROH \longrightarrow CH_4 + R_2CO_3 \quad (b)$$

$$CH_3CH_2OH + 2ROH \longrightarrow CH_4 + 2H_2 + R_2CO_3 \quad (c)$$

and the summation equation is

$$CH_3COOCH_2CH_3 + 4ROH \longrightarrow 2CH_4 + 2H_2 + 2R_2CO_3 \quad (IX)$$

The ethyl acetate used for the experimental determinations was the redistilled Eastman best grade possessing a boiling point of 75°C. A ten cc. portion (8.95 grams) was used in all the runs, and was introduced into the alkali in the customary manner. The temperature of the bath was 450°C and the reaction consumed about seven hours for completion.

The data obtained are included in table VI below.

Table VI

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	4.96	4.56	108.8
II	5.15	4.56	112.9
III	5.15	4.56	112.9

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	3.48	4.56	76.4
II	3.68	4.56	80.7
III	3.68	4.56	80.7

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	8.30	8.95	92.8
II	8.38	8.95	93.6
III	8.46	8.95	94.5

	Run I	Run II	Run III	Theoretical
Volume ratio H_2:CH_4	1.42:1	1.40:1	1.40:1	1:1

Here again is noted a decided increase in the yield of hydrogen over methane as calculated in terms of the derived equation (IX) which calls for hydrogen and methane yields in the ratio of $1H_2$ to $1CH_4$.

While text books of organic chemistry commonly postulate that a general method for the preparation of methane is based upon the interaction of sodium acetate and sodium hydroxide according to the equation

$$CH_3COONa + NaOH \longrightarrow CH_4 + Na_2CO_3$$

(which is an example of a type of reaction involving acidic dissociation), it has been observed that the evolution of hydrogen also accompanies that of methane, but no explanation has been offered for the evolution of hydrogen.

By extending the type reaction mechanism to all of the hydrogen atoms of the ethyl acetate molecule exclusive of those in the methyl component of the ethyl radical, the following equation (B) is readily derived:

$$CH_3COOCH_2CH_3 + 8ROH \longrightarrow CH_4 + 6H_2 + 2R_2CO_3 + R_4CO_4 \quad (IXB)$$

Accordingly, the concurrence of reactions represented by equations (A) and (B) suffices to explain the concomitant liberation of both hydrogen and methane but it is not feasible, since the products of both reactions (A) and (B) are hydrogen, methane and carbon dioxide to make calculations as to the extent of the concurrence of these reactions as has been done in other concurrent reactions wherein either hydrogen or methane are liberated according to one reaction while both hydrogen and methane were liberated according to the second. Such has been shown to be the case of glycerine, dextrose, levulose and cellulose.

It is of further significance to add that in previous investigations conducted independently in this laboratory by Otto (18) and by Williams, (5) attention has been called to the fact that not only acetic acid, but also methyl acetate upon decomposition with fused caustic alkalies gave yields of hydrogen not explained in terms of the proposed reaction mechanism but which now may be explained by extending, as above noted, the type reaction to other hydrogen atoms of the molecules of these compounds.

G. Diethyl Carbonate

The next compound studied was the diethyl ester of carbonic acid which is usually prepared by reacting phosgene with ethyl alcohol

$$CO(Cl)_2 + 2HOC_2H_5 \longrightarrow CO(OC_2H_5)_2 + 2HCl$$

This compound may be expected to react with fused anhydrous caustic alkali in accord with the general type equation in the following manner:

$$CO(O\,C_2H_5)_2 + 2ROH \longrightarrow CO(O\,R)_2 + 2C_2H_5OH \qquad (a)$$

and the ethyl alcohol will then react in its customary manner:

$$2C_2H_5OH + 4ROH \longrightarrow 2CH_4 + 4H_2 + 2R_2CO_3 \qquad (b)$$

The summation of these equations leads to equation X.

$$\Sigma(a)(b) \quad CO(OC_2H_5)_2 + 6ROH \longrightarrow 2CH_4 + 4H_2 + 3R_2CO_3 \qquad (X)$$

The experimental procedure employed was similar to that of the preceding esters studied. The redistilled purest Eastman ethyl carbonate was employed, the portion boiling between 124°C and 126°C was used. A ten cc. portion (9.76 grams) was employed in each run. The temperature of the bath was kept at 450°C and the reaction consumed about six hours.

The data obtained are tabulated in Table VII below:

Table VII
Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	6.46	7.41	87.2
II	6.45	7.41	87.0
III	6.40	7.41	86.4

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	3.34	3.71	90.0
II	3.74	3.71	100.7
III	3.70	3.71	99.7

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	9.74	10.91	89.3
II	9.90	10.91	90.8
III	9.58	10.91	87.8

	Run I	Run II	Run III	Theoretical
Volume ratio H:CH_4	1.93:1	1.73:1	1.73:1	2:1

It is to be noted that in this case the percentage yield of methane exceeded that of hydrogen, the ratio being 1.8:1 instead of 2:1 (hydrogen to methane) as the theory demands. This is not analogous to the data obtained in the preceding cases, where the yield of hydrogen was somewhat in excess of that of methane, which is in general to be expected owing to the increased solubility of methane over that of hydrogen.

The data however, apart from this discrepancy, indicate that diethyl carbonate reacts with fused caustic alkali in a manner demanded by the specific reaction mechanism.

H. Ethyl ortho-formate

This compound is one of the few stable compounds of the hypothetical ortho-formic acid $H-C(OH)_3$ which has never

been isolated. The ester is prepared by the action of ethyl alcohol upon chloroform

$$HCCl_3 + 3HOC_2H_5 \longrightarrow 3HCl + H\text{-}C(OC_2H_5)_3$$

Compounds of this type have never before been studied in the light of their reaction with fused anhydrous caustic alkalies.

The specific reaction mechanism may be postulated in accord with the general type equation by assuming preliminary hydrolysis of the ester and the subsequent reaction of the ethyl alcohol with the alkali in the characteristic manner. The residue, assuming it to be a tri sodium or tri potassium ortho formate then reacts to form one molecule of hydrogen and a molecule of alkali ortho carbonate, thus

$$H\text{-}C(O\text{-}CH_2CH_3)_3 + 3ROH \longrightarrow H\text{-}C(O\text{-}R)_3 + 3C_2H_5OH \qquad (a)$$

$$3C_2H_5OH + 6ROH \longrightarrow 3CH_4 + 6H_2 + 3R_2CO_3 \qquad (b)$$

$$H\text{-}C(O\text{-}R)_3 + ROH \longrightarrow H_2 + R_4CO_4 \qquad (c)$$

The summation of these equations leads to

$$\leq (a)(b)(c) \quad H\text{-}C(O\text{-}CH_2CH_3)_3 + 10ROH \longrightarrow 3CH_4 + 7H_2 + 3R_2CO_3 + R_4CO_4 \qquad (XI)$$

For the experimental procedure the purest redistilled Schering-Kahlbaum product boiling at 145°C was used. A ten cc. portion (8.87 gm.) was employed in each run, and the reaction was carried out at a temperature of 50°C.

The data obtained are listed in Table VIII.

Table VIII

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	3.48	9.39	37.1
II	3.71	9.39	39.4

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	4.50	4.02	112.0
II	4.41	4.02	110.0

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	7.16	10.54	67.9
II	6.78	10.54	64.3

It is quite evident that the data above tabulated can in no sense be regarded as confirming the derived equation (XI); since, however, the data for the two sets of duplicate runs check, it follows that another summation equation more concordent with the data is derivable through some other specific reaction mechanism based upon principles demanded by our fundamental type equations. Such a summation equation may be derived according to the following reaction mechanism scheme.

The first intermediate step is the occurrence of a

type reaction wherein the three methyl radicals of the three ethyl groups are liberated as three molecules of methane accompanied by the liberation of one molecule of hydrogen in conformity with the equation:

$$H-C(-O-CH_2-CH_3)(-O-CH_2-CH_3)(-O-CH_2-CH_3) + 4ROH \longrightarrow 3CH_4 + H_2 + R-O-C(-O-CH_2-O-R)(-O-CH_2-O-R)(-O-CH_2-O-R) \quad (a')$$

Inspection of the latter complex molecule immediately reveals that it is equivalent to one molecule of alkali ortho carbonate and three molecules of formaldehyde. Accordingly it may be assumed that in the decomposition of this complex by heat, it may be resolved into one molecule of alkali ortho carbonate and three molecules of formaldehyde which in turn may polymerize to one molecule of lactic acid.

It would be illogical to assume that the caustic alkalies react with formaldehyde according to the previously established equation

$$CH_2O + 2ROH \rightarrow R_2CO_3 + H_2 \quad \text{(Fry and Schulze)}$$

because the occurrence of such a reaction would increase the yield of hydrogen much above that actually obtained. It is therefore better to assume that the above noted complex is resolved into one molecule of alkali ortho carbonate and one molecule of lactic acid.

These changes are embodied in the equation

$$R-O-C(-O-CH_2-O-R)(-O-CH_2-O-R)(-O-CH_2-O-R) \longrightarrow R_4CO_4 + CH_3CHOHCOOH \quad (b')$$

Now since it has been shown in the author's M.A. thesis that lactic acid reacts with fused caustic alkalies in

conformity with the following equation

$$CH_3CHOHCOOH + 4ROH \longrightarrow CH_4 + 2H_2 + R_2CO_3 + H_2O \quad (c')$$

it follows that another complete equation for the interaction of ethyl ortho formate with fused caustic alkalies is herewith derivable by summing the three above intermediate equations.

$$H-C(O-CH_2-CH_3)_3 + 4ROH \rightarrow 3CH_4 + H_2 + R-O-C(O-CH_2-O-R)_3 \quad (a')$$

$$R-O-C(O-CH_2-O-R)_3 \longrightarrow R-O-C(O-R)_3 + CH_3CHOHCOOH \quad (b')$$

$$CH_3CHOHCOOH + 4ROH \rightarrow CH_4 + 2H_2 + 2R_2CO_3 + H_2O \quad (c')$$

$$\Sigma (a')(b')(c') \quad H-O-C(O-CH_2-CH_3)_3 + 8ROH \rightarrow 4CH_4 + 3H_2 + 2R_2CO_3 + R_4CO_4 + H_2O \quad (XII)$$

The yields of methane, hydrogen and carbon dioxide are retabulated and recalculated on the basis of the newly developed equation and are tabulated in Table IX below:

Table IX

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	3.48	4.02	86.6
II	3.71	4.02	92.3

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	4.50	5.36	84.0
II	4.41	5.36	82.3

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	7.16	7.90	90.6
II	6.78	7.90	85.5

	Run I	Run II	Theoretical
Volume ratio $CH_4:H_2$	1.29:1	1.20:1	1.33:1

Since the yields of methane, hydrogen and carbonate, within the limits of experimental error, are in agreement with the yields required by the newly proposed summation equation, it may be concluded that the assumed intermediate reactions are not only valid but also throw new light upon the explanation of the interaction of ethyl ortho formate with fused caustic alkalies.

I. Ethyl Lactate

The interaction of lactic acid and sodium lactate with fused anhydrous caustic alkalies has been previously investigated, (6) and the data so obtained has indicated that these compounds conform in their behavior with the general type equation I above.

Hence the ethyl ester of lactic acid may be expected to react analogously to the esters of simple organic acids and to yield products as demanded by the specific reaction mechanism indicated below.

$$CH_3CHOHCOO\text{-}CH_2\text{-}CH_3 + ROH \longrightarrow CH_3CHOHCOOR + CH_3CH_2OH \qquad (a)$$

$$CH_3CHOHCOOR \longrightarrow CH_3CHO + HCOOR \qquad (b)$$

$CH_3CH_2OH + 2ROH \longrightarrow CH_4 + 2H_2 + R_2CO_3$ (c)

$CH_3CHO + 2ROH \longrightarrow CH_4 + H_2 + R_2CO_3$ (d)

$HCOOR + ROH \longrightarrow H_2 + R_2CO_3$ (e)

The summation of all these partial equations being

$\leq (a)(b)(c)(d)(e)$ $CH_3CHOHCOOC_2H_5 + 6ROH \longrightarrow 2CH_4 + 4H_2 + 3R_2CO_3$ (XIII)

This ester is quite stable boiling at 154°C and may be expected to yield satisfactory results when reacted with anhydrous caustic alkalies.

The pure Eastman product was redistilled and the fraction boiling between 152°C and 154°C was used in the runs.

In several preliminary runs the customary amount employed in other investigations, namely 10 cc., was used, but this was found to consume an inconveniently long period of time, and the intense radiation of the furnace, impinging upon the Walther dropping funnel for a length of time resulted in several accidents which precluded successful determinations. The sample was then limited to 5 cc. or 5.14 grams. This was dropped into the fused alkali at a temperature of 500°C. The time required for the completion of the reaction was seven to eight hours.

The results are included in Table X below.

Table X

Hydrogen

Run	H_2 found Liters 0°/760 mm.	H_2 calculated Liters 0°/760 mm.	Per cent yield
I	3.75	3.91	95.9
II	3.74	3.91	95.7

Methane

Run	CH_4 found Liters 0°/760 mm.	CH_4 calculated Liters 0°/760 mm.	Per cent yield
I	1.68	1.96	85.7
II	1.65	1.96	84.2

Carbon Dioxide

Run	CO_2 found gms.	CO_2 calculated gms.	Per cent yield
I	5.50	5.75	95.6
II	5.58	5.75	97.0

	Run I	Run II	Theoretical
Volume ratio H_2:CH_4	2.2:1	2.3:1	2:1

The data clearly indicate that ethyl lactate reacts with caustic alkali in conformity with the specific reaction mechanism scheme indicated by equation XIII.

V. GENERAL SUMMARY AND CONCLUSIONS

An extension of the previously developed type equations (I)(II) and (III) involving the acidic dissociation of caustic alkalies to the hydrogen, methyl and ethyl radicals of a variety of carbon compounds, has led to the formulation of reaction mechanism schemes. By summation of the intermediate equations postulated in these schemes, a final equation for the reaction of each compound investigated has been derived and confirmed within the limits of experimental error with the data obtained.

The following specific conclusions are noted:

(1) In each compound investigated the final product of oxidation was the alkali carbonate only.

(2) In conformity with the previously developed rule, hydrogen and methyl radicals when attached to carbon atoms which were in turn united to oxygen atoms were invariably liberated as hydrogen and methane.

(3) Ethyl radicals, so united in the compounds investigated did not lead to the formation of ethane but yielded hydrogen and methane.

(4) The fact that sodium oxalate, which does not contain hydrogen atoms, yielded hydrogen is conclusive evidence for the acidic dissociation of alkali hydroxide. The latter so reacted to yield hydrogen compounds intermediately which in turn gave free hydrogen.

(5) In the investigations with the six ethyl esters

investigated, the final equation for the reactions occurring were derived by applying the general type equations to each hydrogen and methyl radical in the compound. They were quite in conformity with the data obtained, with the exception of ethyl ortho formate which gave an abnormally high yield of methane and an abnormally low yield of hydrogen and carbonate.

(6) This behavior of ethyl ortho formate was only apparently abnormal and it was explained in terms of the type reaction and rule by an equivalently parallel reaction mechanism scheme which indicated the intermediate formation of lactic acid. Knowing the reaction for lactic acid, another summation equation was derived and found to be in conformity with the experimental data.

(7) The liberation of hydrogen when sodium acetate or ethyl acetate interacts with fused caustic alkalies has been noted but is not explained in the literature. The present theory not only explains the regularly recorded reactions but also accounts for the liberation of hydrogen when applied to all of the hydrogen and methyl radicals of the molecule.

Since the experimental data of this thesis, in addition to previously published results in this field, confirm the derived equations, it may be concluded a priori that the proposed reaction mechanism schemes are further substantiated.

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