INTERACTION OF ALCOHOLS WITH ALKALIES UNDER AUTOGENEOUS PRESSURE

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Carrol[1] and Fry[2] *et al.* have shown that when ethyl alcohol reacts with sodium hydroxide at 250–280° C. and at atmospheric pressure, the yield of sodium acetate is low while that of sodium carbonate is comparatively high. Weizmann and Garrard[3] have carried out the reaction at 40–50 atmospheres and at a temperature of 250–260° C., obtaining a yield of about 25% on the basis of sodium hydroxide taken. Reid, Worthington and Larchar[4] on the other hand have claimed an yield of 60–95% by working at a pressure of 400 atmospheres and at 320° C. Stephenson and Pelton[5] have patented processes involving the reaction of alkali with a number of alcohols. Stochiometric relationship of this reaction (equation 1) shows that two moles of hydrogen are liberated when sodium acetate is formed. The reaction should, therefore, proceed more easily at atmospheric pressure. But the literature cited above indicates the reverse process. The present work is undertaken to study the mechanism of this anomalous reaction.

EXPERIMENTAL

The apparatus consists of a high pressure bomb (1·35″ i.d.; 3·65″ o.d.) made of molybdenum steel having a capacity of 380 c.c. (Fig. 4) tested to withstand pressures up to 1,000 atms. at 500° C. The bomb is placed in an electric furnace, the temperature of which can be controlled with a Sunvic regulator correct to ±3° C. The top cover of the bomb is connected with the gas inlet and the pressure gauge, while the gas outlet is situated at the bottom. Connections are made using Aminco stainless steel tubing ¼″ o.d. and 1/16″ i.d.

The reactants, *viz.*, sodium hydroxide, alcohol and water are first mixed in a stainless steel tube 195 c.c. in capacity. The tube is placed in the bomb, the top cover of which is then closed. The apparatus is checked for leaks with pure nitrogen from the cylinder, the pressure of which could be enhanced with the aid of the booster pump. The nitrogen is then let out and the bomb heated to the required temperature. After the reaction, it is cooled and the gaseous products are discharged through spiral glass condensers cooled to −15° C., into the gas holder containing brine and from which the sample of the gas is taken and analysed employing Orsat's apparatus. The contents of the stainless steel tube are analysed for sodium acetate, sodium hydroxide and sodium carbonate after making up to a known volume. Sodium acetate is estimated by taking an aliquot of the solution, acidifying with phosphoric acid and steam distilling

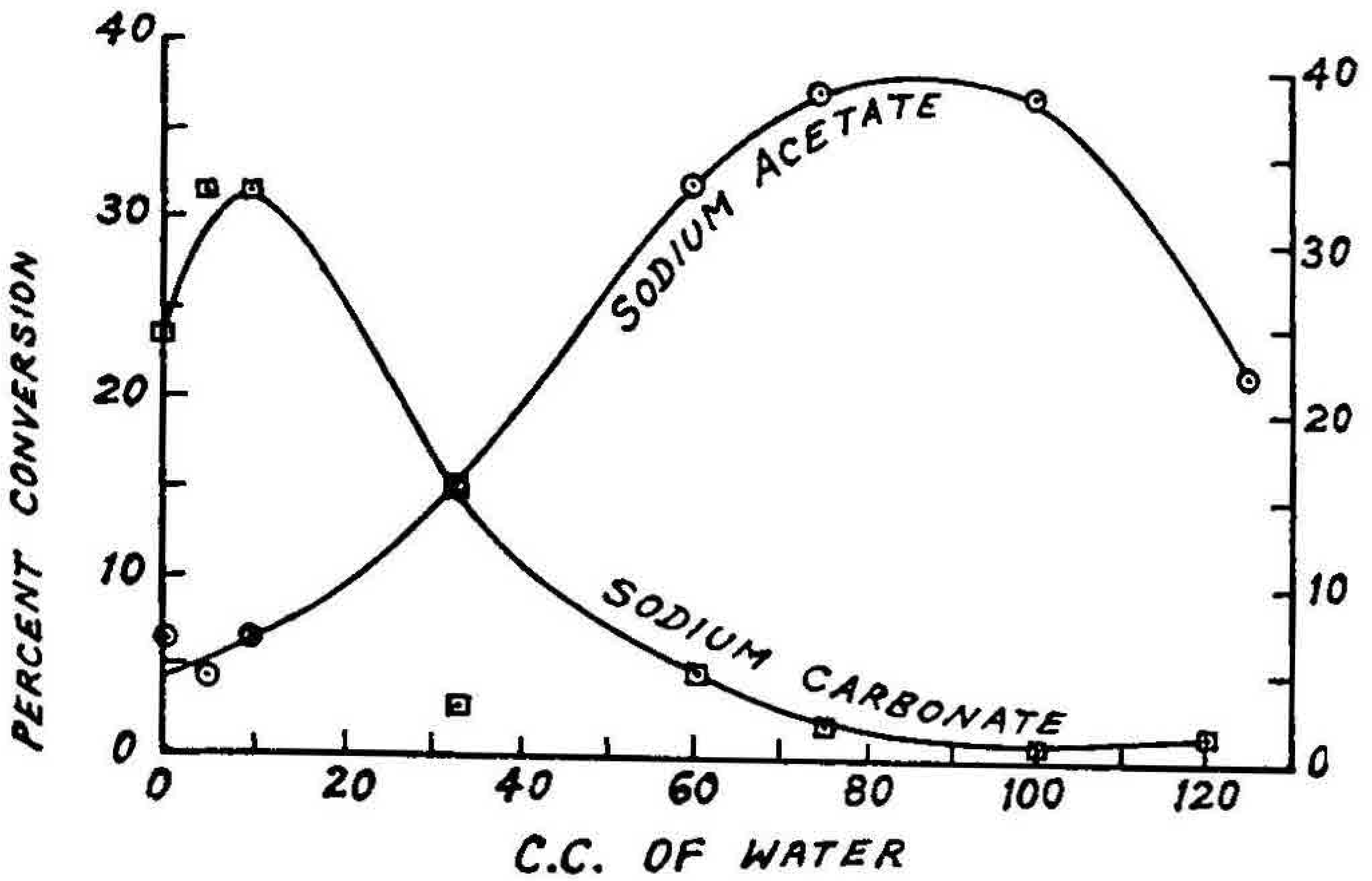


FIG. 1. Effect of water on the reaction between alcohol and sodium hydroxide: NaOH = 20g. Alcohol = 23g. Temp. = 350° C. Time of Reaction = 2·5 hrs.

the acetic acid which is then titrated against standard alkali. Sodium hydroxide and carbonate are estimated in separate portions of the solution with standard acid.

Influence of water on the reaction

It was pointed out by Reid *et al.*[4] that water was beneficial for the reaction but no detailed study of this, seems to have been made. The influence of water on the reaction has, therefore, been investigated by us and the results obtained are presented in Fig. 1, where the amount of water is plotted against percentage conversion of sodium hydroxide to sodium acetate and to sodium carbonate. It is seen from the figure that as the amount of water increases in the system, the percentage conversion of sodium hydroxide to acetate is first enhanced but when the water content is beyond 90 gm. there is a decrease in acetate formation. The production of sodium carbonate on the other hand is first enhanced slightly but when the water content is increased beyond 10 gm. there is a fall in the carbonate produced. In subsequent experiments, therefore, 75 c.c. of water was added for every 20 gm. of the sodium hydroxide employed in the reaction.

Influence of temperature on the reaction

The heats of formation of sodium acetate and sodium carbonate are given in equations 1 and 2.

$$CH_3CH_2OH + NaOH \dashrightarrow CH_3COONa + 2\,H_2 \qquad (\Delta H \quad 16{\cdot}26 \text{ Kcal}) \quad (1)$$

$$CH_3COONa + NaOH \dashrightarrow Na_2CO_3 + CH_4 \qquad (\Delta H \quad -14{\cdot}94 \text{ Kcal}) \quad (2)$$

(The ΔH values are calculated from the data available in ref. 6)

The difference in the heats of reaction can be expected to influence the nature of the products formed at various temperatures. Table 1 gives the effect of temperature on the reaction. It is clear that as the temperature increases the production of sodium acetate is also enhanced. At the same time the decomposition of the acetate (reaction 2) proceeds at a higher rate. The temperature for the production of the maximum quantity of the acetate is round about 375° C. It is interesting to note that the formation of the sodium acetate commences at about 250° C. which happens to be slightly above the critical temperature (243·1° C.) for the ethyl alcohol. Similarly at about the critical temperature of water (374° C.) there is the rapid formation of sodium carbonate.

TABLE I

Effect of temperature on the conversion of sodium hydroxide to sodium acetate

Time of reaction = 2·5 hr.

Reactants $\begin{cases} \text{NaOH} = 20\text{ gm.} \\ \text{Alcohol} = 23\text{ gm.} \\ \text{Water} = 75\text{ gm.} \end{cases}$

No.	Temp. ° C.	% conversion of NaOH to acetate	% conversion of NaOH to Na_2CO_3	% unreacted NaOH	Pressure at the end of reaction p.s.i.g.
1	200	..	..	100	300
2	250	3·83	..	94·80	850
3	300	18·87	..	79·05	1,600
4	320	24·26	0·69	72·30	2,200
5	350	38·13	1·71	60·05	3,400
6	375	44·24	12·00	39·80	5,250
7	400	41·39	32·35	23·55	5,600

Effect of mol. ratio of alcohol to sodium hydroxide

From the equation (1) it is evident that the reaction would require equivalent amounts of alcohol and sodium hydroxide. But it has been reported by Reid *et al.*[4] that excess of alcohol is necessary for the reaction. A detailed investigation has been carried out to determine the influence of alcohol on the reaction. Table II gives the data obtained.

TABLE II

Effect of mol. ratio of alcohol to sodium hydroxide on the reaction

Reactants { Alcohol = 23 gm. (0·5 mole)
Water = 75 gm. (4·2 moles)
Temperature = 375° C. Time = 2·5 hours

No.	Amount of sodium hydroxide taken	Mols. EtOH/NaOH	Pressure at the end of reaction p.s.i.g.	% conversion of NaOH to Na acetate	% conversion of NaOH to Na_2CO_3	% un-reacted NaOH	gm. of NaOH to Na_2CO_3
1	0·0	∞	4,000	0·00	0·00	0·00	0·00
2	5·0	4·00	4,000	96·75	2·70	..	0·13
3	7·5	2·66	4,600	96·24	1·60	..	0·12
4	10·0	2·00	4,700	70·20	7·89	16·70	0·79
5	15·0	1·33	4,400	63·42	11·66	24·26	1·70
6	20·0	1·00	5,250	44·24	12·00	39·80	2·40
7	30·0	0·66	3,800	22·31	8·16	67·73	2·45
8	40·0	0·50	3,300	10·50	4·57	83·66	1·83

It is noticed that at a mole ratio of alcohol to sodium hydroxide of 2·66 and above, almost quantitative conversions are achieved. Below this value, sodium carbonate formation is favoured. Hence the optimum ratio for alcohol to sodium hydroxide for the production of sodium acetate can be taken as 2·7.

Influence of time on the progress of reaction

It was noticed during the preliminary studies that after the attainment of the required temperature, the pressure of the system continued to increase slowly. Fig. 2 gives the effect of time on the reactions (1) and (2). It is seen that the sodium acetate in the product goes on increasing slowly for about one hour, after which it remains more or less constant. Similarly, the production of sodium carbonate attains the maximum value in about two hours. Time of contact is particularly important at atmospheric pressure since the acetate formed reacts with excess of sodium hydroxide to form sodium carbonate and methane. At higher pressures, however, the reaction (2) is checked to a large extent. It can be concluded that a period of 2–2½ hours is adequate for the completion of the reaction.

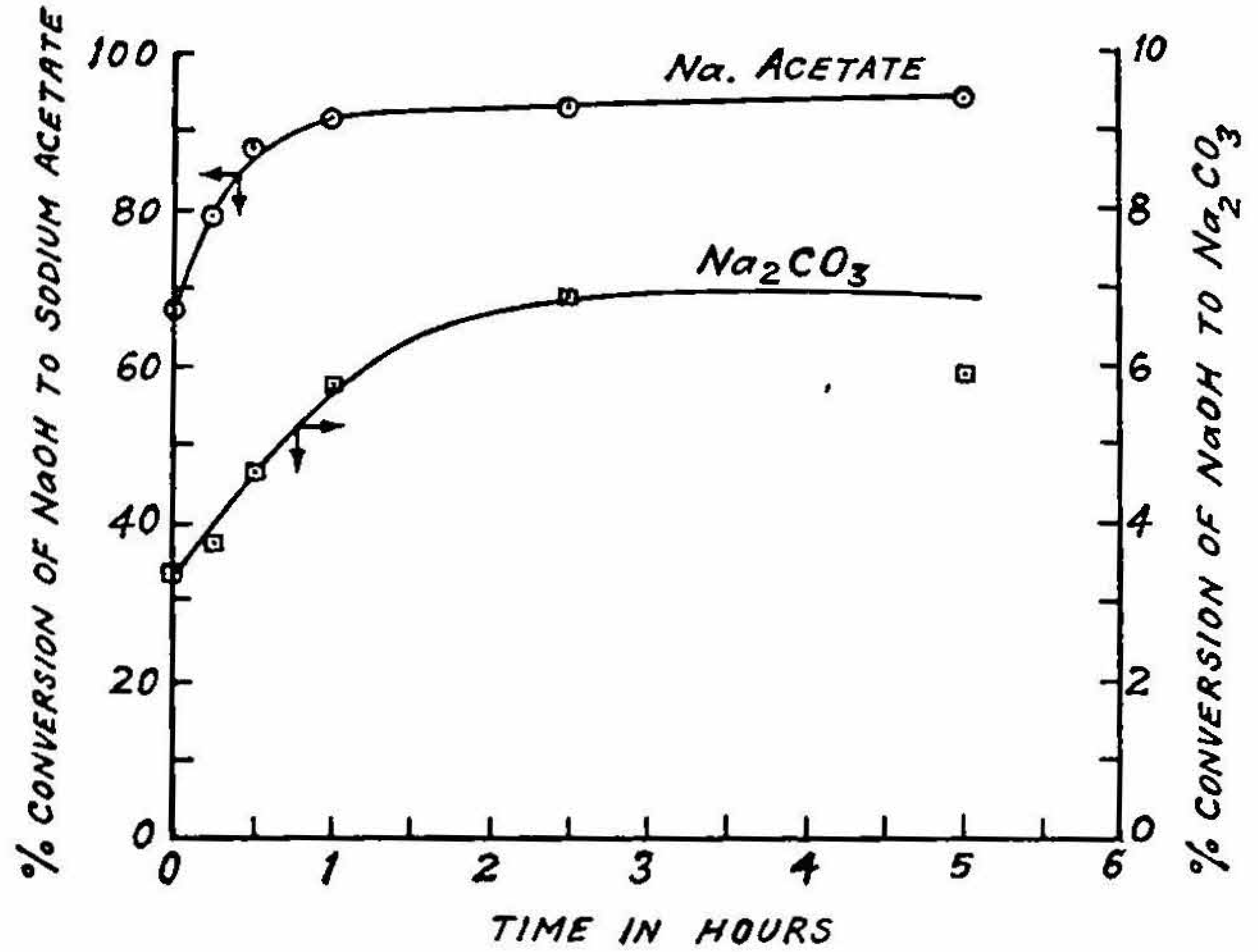


FIG. 2. Effect of time on the production of sodium acetate and carbonate. NaOH= 7·5 g. Alcohol=23 g. Water=75 c.c. Temp.=375° C.

Influence of the quantities of the reactants on the production of sodium acetate

In Table II it has been shown that the maximum yield of acetate is obtained by taking 7·5 gm. sodium hydroxide, 23 gm. alcohol and 75 c.c. of water. Maintaining this ratio of the reactants, the reaction was carried out reducing the quantities of the reactants in order to find out the extent of the production of the acetate on the total pressure and the results are given in Table III.

TABLE III

Effect of the quantities of the reactants on the production of the acetate

$$1 \text{ Unit} \begin{cases} \text{NaOH} = 7\cdot5 \text{ gm.} \\ \text{Alcohol} = 23 \text{ gm.} \\ \text{Water} = 75 \text{ gm.} \end{cases}$$

Temperature = 375° C. Time = 2·5 hours

No.	Reactants (unit)	Pressure developed in p.s.i.g.	% NaOH converted to sodium acetate	% NaOH converted to Na_2CO_3	% NaOH unreacted
1	¼	2,000	34·63	38·25	24·46
2	½	3,300	79·22	8·55	10·55
3	¾	4,000	86·55	8·40	4·01
4	1	4,600	96·24	1·56	Nil

These results indicate that with the lowering of the quantities of the reactants, both the overall reaction and the production of sodium acetate get reduced while the amount of sodium carbonate formed is enhanced. The lowering of the overall reaction may either be due to the reduction in the total pressure at the reaction temperature or due to insufficient quantities of alcohol and water in the gaseous phase. The effect of total pressure on the production of sodium acetate was, therefore, studied employing hydrogen and nitrogen in the gaseous phase.

Influence of pressure on the nature of the reaction

In these reactions 7·5 gm. of sodium hydroxide and 23 gm. of alcohol were subjected to various pressures of hydrogen at 375° C. for a period of 2½ hours and the products obtained are given in Table IV.

TABLE IV

Effect of pressure on the reaction between sodium hydroxide and alcohol

Reactants { NaOH = 7·5 gm.
Alcohol = 23 gm.

Temperature = 375° C. Time = 2·5 hours

No.	Gas or vapour in the bomb	Initial pressure p.s.i.g.	Final pressure p.s.i.g.	NaOH to NaAc %	NaOH to Na_2CO_3 %	NaOH unreacted %
1	Nitrogen ..	0·00	1,525	6·56	23·63	69·79
2	Hydrogen ..	500	2,400	16·76	15·42	67·51
3	Do. ..	1,000	3,300	19·99	17·92	62·09
4	Do. ..	1,500	4,500	13·65	11·00	75·34
5	Nitrogen ..	1,000	3,250	19·75	18·02	62·23
6	Water (13 gm.)	0·00	2,000	25·50	19·90	54·20
7	Do. + hydrogen	1,000	4,000	23·50	21·40	54·20
8	Water (75 gm.)	0·00	4,600	96·24	1·56	Nil

These results indicate that when the pressure development is only due to water vapour (Experiment 8), the yield of the acetate is the highest while that of the carbonate is the lowest. When the pressure developed is only due to the inert gas, the overall reaction is reduced considerably. The acetate yield is far lower while the corresponding yield of the carbonate is enhanced. When small quantities of water (13 gm.) are added to the reaction mixture both the overall reaction and the acetate formation go up with a simultaneous diminution of the carbonate formed. Building up of pressure with the inert gas without the water vapour does not influence the nature of the products of reaction to any considerable degree. It is thus clear that a high pressure of water vapour is essential for the quantitative production of the sodium acetate.

Reaction with other alcohols

The following optimum conditions were employed to study the reaction between sodium hydroxide and other alcohols: Alcohol: sodium hydroxide = 2·7, water = 75 gm., temperature = 375° C. and time of reaction = one hour.

The results obtained with the normal alcohols are given in Table V.

TABLE V

Formation of fatty acid salts from corresponding alcohols

No.	Alcohol used		No. of carbon atoms	Critical temp. of		% sodium hydroxide converted into		
				Alcohol ° C.	Acid ° C.	Fatty acid salt	Na_2CO_3	Unreacted
1	Methyl alcohol	..	1	240·0	..	Nil	100	Nil
2	Ethyl ,,	..	2	243·1	321·6	96·24	1·56	,,
3	*n*-propyl ,,	..	3	263·7	339·5	94·28	3·90	0·86
4	*n*-butyl ,,	..	4	287·0	355·0	56·32	7·52	36·16
5	*n*-amyl ,,	..	5	348·0	379·0	46·10	5·37	45·95
6	*n*-hexyl ,,	..	6	..	..	47·70	6·03	43·33
7	*n*-heptyl ,,	..	7	365·0	..	26·20	14·48	59·32
8	*n*-octyl ,,	..	8	385·0	..	23·36	13·11	63·53
9	Iso-propyl ,,	..	3	235·0	..	..	2·47	96·90
0	Iso-amyl ,,	..	5	307·0	..	100·0	..	..

It is seen from Table V that the conversion of the alcohol into the acid diminishes with an increase in the number of carbon atoms except in the case of methyl alcohol where the formation of the carbonate is quantitative. The amount of the carbonate in other cases increases, in general, with an increase in the number of carbon atoms in the alcohol. It is interesting to note that iso-amyl alcohol gives practically 100% conversion into the fatty acid, while iso-propyl alcohol gives practically no yield of the corresponding acid. These results also indicate that in the case of normal alcohols, an increase in the critical temperature of the alcohol brings about a diminution in the production of the acid. The number of carbon atoms in the normal alcohol has been plotted *vs.* log fatty acid formed in Fig. 3 and a linear relationship is obtained except in the case of methyl alcohol.

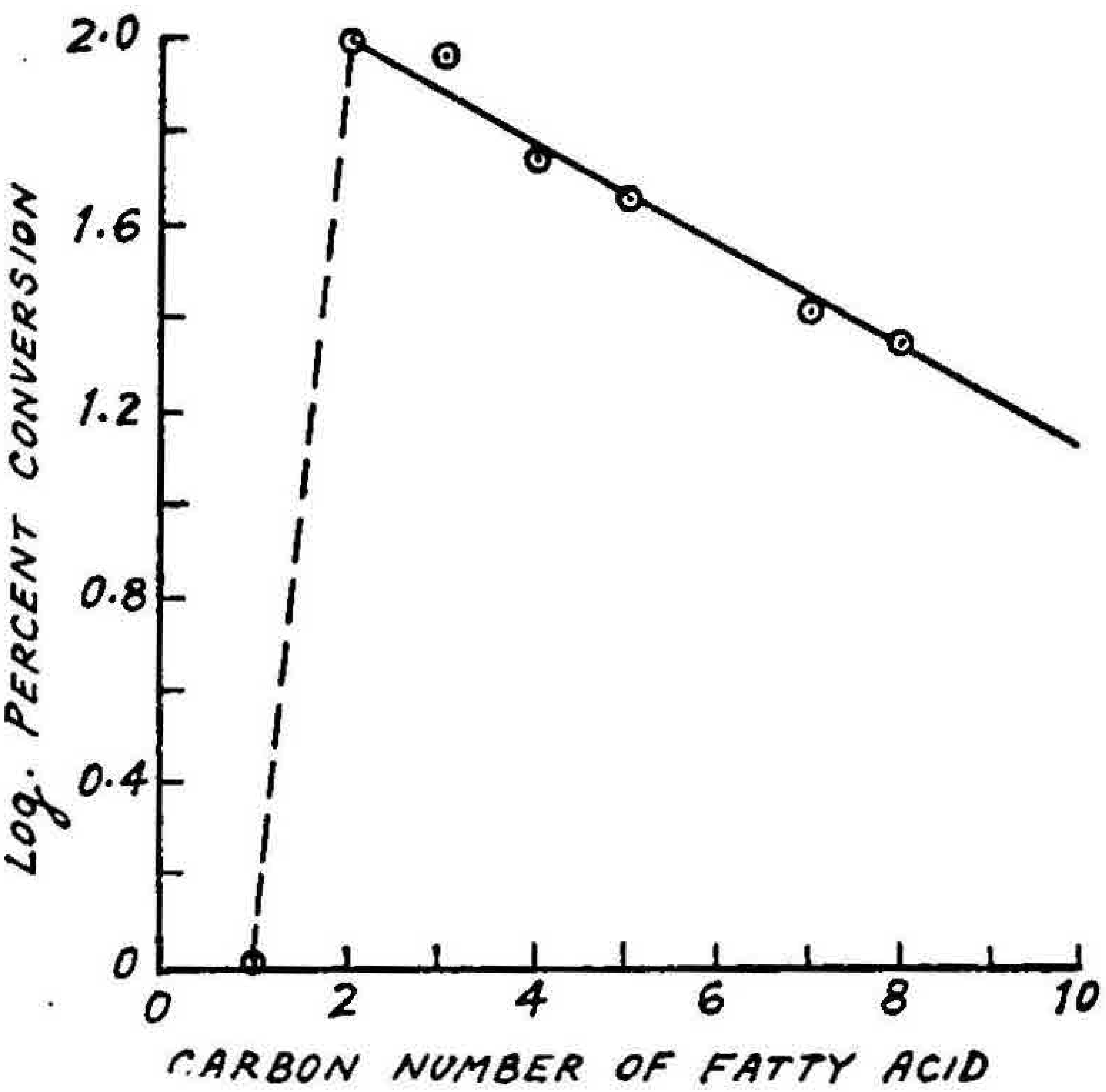


FIG. 3. Per cent. conversion of NaOH to corresponding fatty acid salt.

Methyl alcohol behaves very differently from other alcohols with respect to its reaction with alkali. Results of Table V indicate that sodium carbonate is the only product of the reaction. A detailed investigation on the effect of temperature for various intervals was carried out and the results are given in Table VI.

TABLE VI

Reaction between methyl alcohol and sodium hydroxide

Reactants { water 75 gm.
methyl alcohol 23 gm.
sodium hydroxide 7·5 gm.

Expt. No.	Temp. ° C.	Duration of expt. hr.	Initial pressure of hydrogen p.s.i.g.	% sodium hydroxide		
				Converted into formate	Converted into Na_2CO_3	Unreacted
1	250	1	Nil	1·5 (by diff.)	3·52	95·30
2	300	1	,,	11·18	14·05	69·70
3	325	1	,,	6·03	64·60	27·40
4	375	1	,,	Nil	100·00	Nil
5	300	4	,,	10·05	21·32	66·76
6	325	4	,,	9·41	81·00	8·64
7	300	1	1,000	6·84	6·03	87·20
8	325	1	1,000	9·14	42·30	48·40

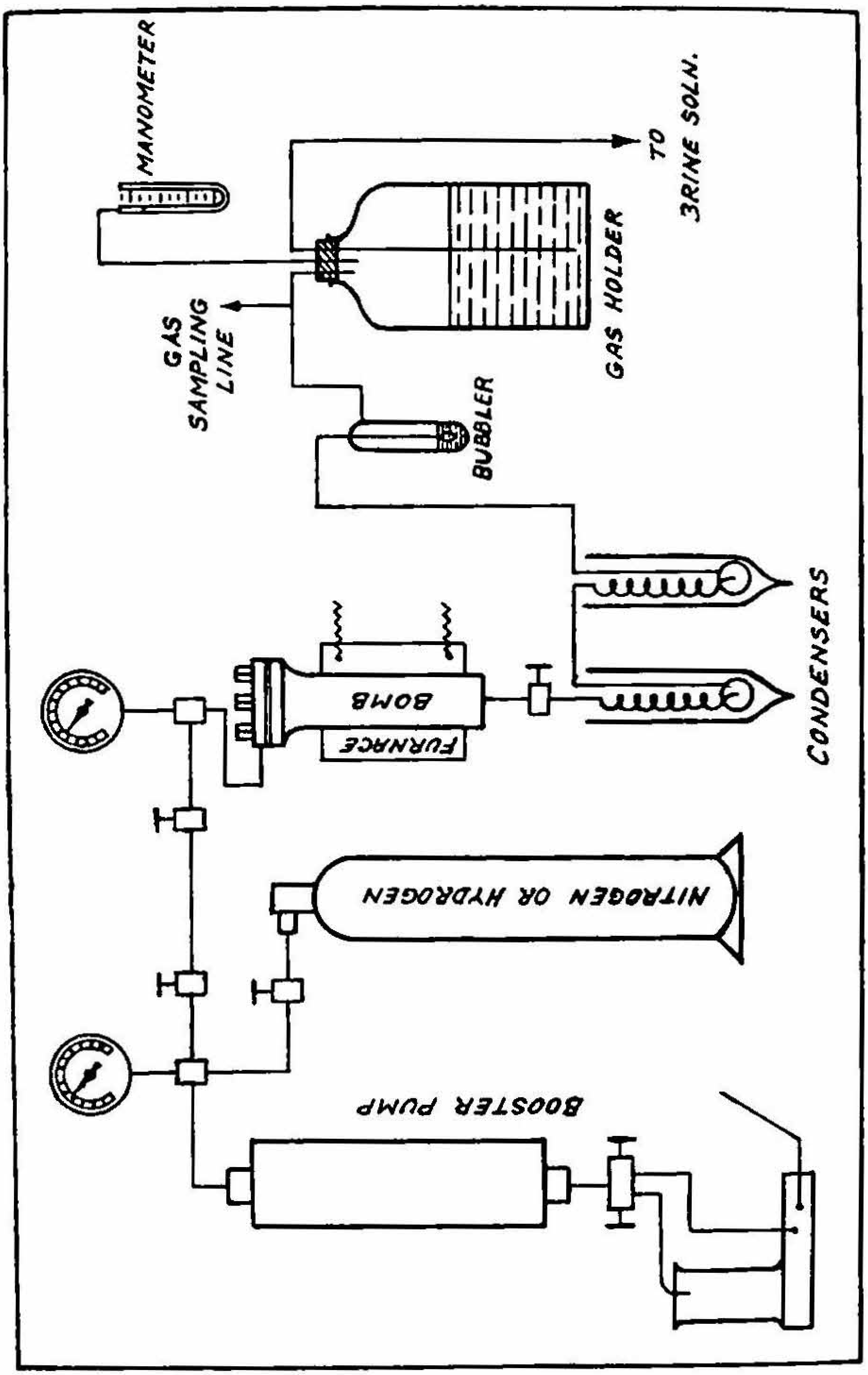

MANOMETER
TO BRINE SOLN.
GAS SAMPLING LINE
GAS HOLDER
BUBBLER
BOMB
FURNACE
CONDENSERS
NITROGEN OR HYDROGEN
BOOSTER PUMP

FIG. 4

These results indicate that at low temperatures (below 250° C.) there is very little reaction between the alcohol and sodium hydroxide. When the temperature is raised to 300° C. about 30% of the hydroxide reacts yielding nearly equal quantities of the formate and the carbonate. If the reaction is allowed to take place at this temperature for four hours, the yield of the carbonate increases to 21%, while that of the formate is retained practically at the same level (10%). This indicates that the formate formed is getting decomposed into the carbonate. When the bomb is filled with hydrogen (Experiments 7 and 8) the total yield of both the formate and the carbonate gets diminished. As the temperature is raised to 325° C., the percentage of the carbonate is greatly enhanced and when the interval of the reaction is increased to four hours, the carbonate formed is nearly 81% while the formate level is maintained at about 9%. As in the previous case, the presence of hydrogen diminishes the overall reaction between the alcohol and the hydroxide.

Decomposition of sodium acetate at elevated temperatures and pressures

The present work indicates that when the reaction temperature is increased, the yield of sodium carbonate is correspondingly enhanced (Table I); this is

TABLE VII

Decomposition of sodium acetate at elevated temperatures and pressures

Reactants:
(1–4) 20 gm. $CH_3COONa\ 3\ H_2O$ + hydrogen
(5) 20 gm. CH_3COONa anhydrous + hydrogen
(6) 15·3 gm. ,, + nitrogen
(7) 15·3 gm. ,, + 75 gm. water + 23 gm. alcohol
Reaction temperature = 350° C. (375° C. in Expt. 7)
Reaction time = 2·5 hours

Expt. No.	Initial pressure p.s.i.g.	Pressure of reaction p.s.i.g.	Pressure after cooling to room temp. p.s.i.g.	$\frac{Na_2CO_3}{\text{Na-acetate}} \times 100$
1	400	1,400	410	0·76
2	600	1,800	600	0·53
3	1,000	2,600	1,000	0·66
4	1,500	3,700	1,500	0·59
5	2,350	4,850	2,350	8·58
6	2,350	5,425	2,350	13·44
7	0·0	4,100	200	0·0

also true for the diminution in the total amount of the reactants (Table III). The tendency for the increased yield of sodium carbonate is also evident when the quantity of sodium hydroxide in the reaction mixture is enhanced (Table II). Very often the yield of sodium carbonate is enhanced at the cost of sodium acetate (Table I, Experiments 6 and 7). It is therefore necessary to find out the extent of decomposition when sodium acetate is subjected to high pressure conditions. The results are given in Table VII above.

It is evident from the results that hydrated sodium acetate undergoes very little decomposition when heated in presence of hydrogen (1,400–3,700 p.s.i.g.). But when the anhydrous salt is subjected to heating the decomposition of the acetate into carbonate is slightly enhanced. The substitution of hydrogen by nitrogen does not in any way alter the nature of the reaction products. The acetate is also quite stable when heated in presence of water and alcohol at 375° C. for 2½ hours. It is thus clear that in absence of sodium hydroxide, the acetate is thermally stable when heated to 375° C.

DISCUSSION AND CONCLUSION

The reaction of alcohol with alkali is explained by Carrol[1] by postulating the formation of the aldehyde followed by the production of sodium acetate, the ketene or the free radical being the intermediate product.

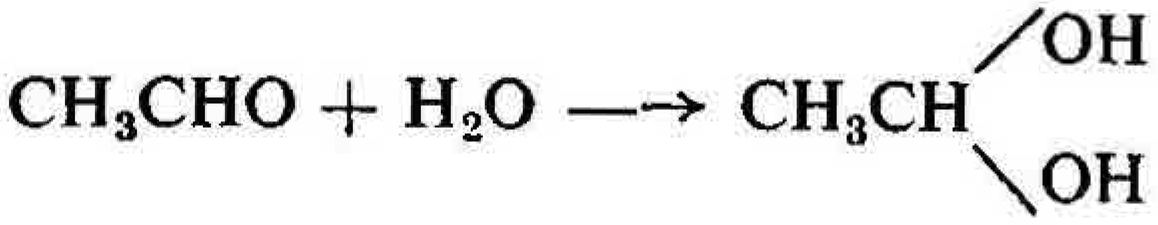
On the basis of these reactions, it is not possible to explain the influence of water on the production of sodium acetate investigated in the present work (Fig. 1). In addition to this, neither the ketene nor the free radical was detected in the reaction mixture by Carrol.[1] Fry and co-workers,[2] on the other hand, assume the formation of sodium ethoxide as the first step for the formation of acetaldehyde, the latter giving rise to sodium acetate in presence of sodium hydroxide. In the present work, however, sodium acetate is formed in presence of a large excess of water and it is improbable that sodium ethoxide could be formed in presence of excess of water.

The analysis of the reaction products indicated small quantities of aldehyde. It is, therefore, probable that the first step in the reaction is the conversion of alcohol to acetaldehyde when sodium hydroxide acts as a catalyst for the dehydrogenation.

$$CH_3CH_2OH \xrightarrow[\text{as catalyst}]{\text{NaOH}} CH_3CHO + H_2$$

Studies on the temperature effect indicate that there is very little reaction between alcohol and sodium hydroxide up to a temperature of 250° C. At the optimum temperature of 375° C. it can be expected that both water and alcohol will be in the vapour phase. Since small amounts of aldehyde have been detected in the reaction mixture, it can be presumed that aldehyde formation is the first stage in the reaction. In absence of sodium hydroxide in the reaction mixture, there is very little decomposition of alcohol. It can, therefore, be concluded that alcohol decomposes into aldehyde and hydrogen in the vapour phase in presence of sodium hydroxide catalyst.

In the present work it has been found that water greatly facilitates the formation of sodium acetate (Fig. 1). This is perhaps due to the formation of the acetaldehyde hydrate according to:



$$CH_3CHO + H_2O \longrightarrow CH_3CH\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$$

The formation of the acetaldehyde hydrate is greatly favoured by the high pressure prevalent under the experimental conditions. The hydrate, however, is catalytically decomposed in presence of sodium hydroxide to give hydrogen and acetic acid, the latter being converted into sodium acetate. Sodium acetate can further react with sodium hydroxide to give sodium carbonate and methane.

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

The dehydrogenation of alcohol and of acetaldehyde hydrate appears to be irreversible reactions as these are not affected by pressure. The scheme given above can, therefore, explain the importance of water in the reaction and also the nature of the products obtained.

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