# The Action of Caustic Alkali and of Alkaline Salts on Alcohols[1]

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In this paper two diverse reactions are considered: (1) the dehydrogenation of an alcohol to a sodium salt and (2) the condensation of two molecules of an alcohol to one of double the number of carbon atoms.

$$PrCH_2OH + NaOH \longrightarrow PrCOONa + 2H_2 \qquad (1)$$
$$2EtCH_2CH_2OH \longrightarrow EtCHBuCH_2OH + H_2O \qquad (2)$$
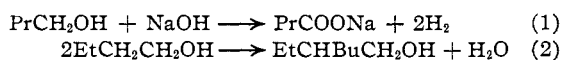
Reaction 1 was discovered by Dumas and Stas.[2] Reaction 2 was investigated thoroughly by Guerbet[3] using various alcohols alone and in mixtures. These reactions are here associated because they so frequently go on in the same mixture. In reaction 2 the attack is predominantly on the beta-carbon but may also be on the alpha. Naturally the alcohol that is formed may also take part in the condensation; thus from butanol a dodecanol and a hexadecanol are obtained along with an octanol but in smaller amounts.

Guerbet dissolved sodium in an excess of an alcohol and heated the mixture in a sealed tube. The sodium alcoholate, which he considered the catalyst, was always completely converted into the corresponding sodium salt. A trace of water in his "anhydrous" alcohols together with the water formed in the condensation furnished the hydroxide required for reaction 1. He was dealing with reaction 1 as well as with 2. If, in carrying out reaction 1, an excess of an anhydrous alcohol is used, a part of the excess is condensed according to 2.

Working at atmospheric pressure, Dumas and Stas were limited to the small amount of an alcohol retained in the pores of the soda-lime at the high reaction temperature. Using sealed tubes Guerbet could operate with only small quantities on account of the excessive pressures due to the hydrogen liberated. Weizmann and Garrard[4] heated 500 g. of n-butanol in which 50 g. of sodium had been dissolved in a steel bomb, venting the hydrogen from time to time. They got high yields of octanol and quantitative conversion of the sodium butylate to butyrate. Substituting sodium hydroxide they found about 80% of it converted to sodium butyrate. With

modern high pressure equipment both reactions become available for preparative purposes. The experiments here recorded were done in the Summer of 1927. The runs made were exploratory and many of them were at such high temperatures that the alcohols formed were largely dehydrated, but considerable was learned about both reactions, enough to put them in a new light and to show how each can be carried out independent of the other. While a sufficient number of experiments was not made to find the best conditions for either reaction, yet the data obtained show the courses of the two reactions and indicate conditions for obtaining satisfactory yields.

Reaction 1 goes rapidly at about 320°; pressures up to 400 atmospheres may develop within a few minutes. Table I gives the results for ethanol, with which most of the runs were made. The conversion to acetate increased from 67 to 98.9%, when the ratio of alcohol to caustic was increased from 1 to 3. The presence of water is beneficial; it suppresses reaction 2 and prevents darkening. Sufficient water to dissolve the product is desirable since this gives a water-white reaction mixture which may be poured out of the bomb and from which the salt crystallizes on chilling. That the reaction goes in the presence of a large amount of water is shown by run 10 in which the free caustic in the product was only 0.08%. Sodium carbonate appeared when the temperature was high or the time long. Ethanol differed from the other alcohols in that it was extensively dehydrated, particularly when much water was present.

With an excess of methanol and water at 350° for one hour, 68% of the alkali went to sodium carbonate, 20.6% to the bicarbonate and 5.7 % to the formate. It is probable that this was overheated and that the formate primarily formed underwent a secondary reaction. The gas evolved contained 97.4% of hydrogen. Several runs with excess anhydrous butanol are given in Table II.

The yield of octanol was larger when potassium hydroxide was used. n-Propyl- and 2-ethylhexanol reacted similarly. With t-butanol about one-fourth of the caustic went to carbonate, no acid was isolated and most of the alcohol was recovered unchanged.

(1) Read at the Dallas American Chemical Society meeting, April, 1938.

(2) Dumas and Stas, Ann., 35, 129–173 (1840).

(3) Guerbet, Ann. chim. phys., [7] 27, 67 (1902); Compt. rend., 146, 298 and 1405 (1908).

(4) Weizmann and Garrard, J. Chem. Soc., 117, 324 (1920).

TABLE I

OXIDATION OF ETHYL ALCOHOL TO SODIUM ACETATE BY SODIUM HYDROXIDE

No. of run	1	2	3	4	5	6	7	8	9	10
Moles EtOH/NaOH	1	2	2.94	1.2	2.0	1.5	1.1	2.0	2.6	2.0
Weight H_2O/NaOH	0	0	0	2.5	5.5	4.5	4.5	3.0	4.0	1.9
Temp., °C.	355	370	330	350	350	380	360	320	380	345
Time. hrs.	3	3	2.75	2.5	3	3	4.25	5.5	0.5	5
% NaOH in prod.	18.2	2.15	0.30	2.52	0.84	0.11	2.15	1.33	.34	0.08
NaOH to acetate	67.0	86.4	98.9	90	94.8	94.5	80.9	89.5	97.9	99.6
NaOH to Na_2CO_3	...	8.6	...	...	...	4.7	5.1	4.3	0.0	0.0
% EtOH to C_2H_4	14.8	6.3	...	...	...	22.1	22.2	22.9	18.0	23.4

TABLE II

CONVERSION OF n-BUTYL ALCOHOL TO SODIUM BUTYRATE BY HEATING WITH CAUSTIC ALKALI

No. of run	1	2	3	4
BuOH, g.	240	240	240	240
Alkali	NaOH	NaOH	NaOH	KOH
Wt. of alkali, g.	50	120	50	80
Molal ratio	2.58	1.07	2.58	2.67
Time, hrs.	4.5	3	20	20
Temp., °C.	330	350	340	350
Acid isolated, %[a]	89	72	70[c]	67
Remaining BuOH to octanol, %[b]	7	...	15	24

[a] The yields of butyric acid are figured on the total butanol put in and do not take into account losses in handling. Distillation showed the acid to be pure except for a small high boiling residue which probably contained an octoic acid.

[b] The yields of octanol are calculated from the original butanol less the amount of butyric acid found.

[c] The butyric acid should have been 94% calculated from the hydrogen evolved and 96% from the sodium hydroxide consumed.

The fact that sodium acetate is used as a condensing agent in Perkin's synthesis and in acetylations suggested that the salts that were formed in Guerbet's experiments may have been responsible, at least in part, for the condensations. It has been found that salts of organic acids do effect condensations according to reaction 2.

The use of a ready made salt has several advantages: the excessive pressures due to the liberation of hydrogen are avoided, none of the alcohol is used up according to reaction 1 and the salt may be reused. Sodium formate with its own weight of butanol at 300–370° for twenty hours gave 12% of an octanol and potassium carbonate only 1%. The results of a number of runs, each with 1000 g. of n-butanol, are given in Table III. The irregular and sometimes serious losses in working up the pasty reaction products together with occasional leaks prevent close comparisons but certain conclusions are clear. Butanol dehydrated to butylene is included in the losses. Run 1 according to Guerbet's method with sodium butylate equivalent to the salts in other runs is notable for the high yield of octanol and low yield of octylene. Perhaps the sodium butylate causes some condensation before it disappears, perhaps the withdrawal of the water necessary for reaction 1, or perhaps the distribution of the nascent sodium butyrate increased the yield of butanol. No one of these assumptions explains why so little of the octanol is dehydrated or condensed to dodecanol. Run 2 shows that potassium hydroxide may be used instead of the butylate with about the same results as are obtained with the equivalent amount of potassium butyrate. This favors

TABLE III

CONDENSATION OF n-BUTANOL TO OCTANOL AND DODECANOL

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Catalyst	NaO-Bu	KOH	Pr-CO_2Na	Pr-CO_2K	Pr-CO_2K	Pr CO_2K	Pr-CO_2Rb	Pr-CO_2K CaO	C_6H_{11}-O_2K	C_8H_{17}-O_2K	Pr-CO_2K	Pr-CO_2K	Pr-CO_2K	Pr-CO_2K
Per cent.	4.5	2.3	5	5	5	5	5	5	5	5	50	50	50	50
Temp., °.	350	325	360	338	343	349	348	350	334	348	400	345	350	335
Time, hrs.	20	20	21	21	21	21	21	21	20	21	2	6	8	3
BuOH recovered	8	59	50	57	40	40	76	...	68	52	17	34	...	41
Loss and C_4H_8	37	6	20	13	12	12	10	...	7	5	29	22	...	38
BuOH to C_8H_{18}	5	9	12	11	19	19	5	...	10	16	30	5.4	...	2.5
BuOH to $C_8H_{18}O$	46	19	12	15	19	19	6.4[a]	13[a]	11	16	14	25	32	13
BuOH to $C_{12}H_{26}O$	4	7	6	5	10	9	2	...	4	11	10	13	...	4.6
Ratio, C_8:C_{12}	12.2	3.9	3.7	5.5	37	4.0	7.4	...	52	3.0	4.2	2.4	...	3.5
% condensed	55	35	30	30	48	47	13	...	25	43	55	44	...	21
% on BuOH used up	60	87	60	70	80	80	57	...	79	89	66	66	...	35

[a] These octanols were low boiling.

the supposition that sodium butylate is a specially active condensing agent. As a whole the experiments show that the salts are efficient condensing agents. Unfortunately they are also dehydrating agents and much of the octanol may be destroyed. It is probable that at a lower temperature and with a shorter time considerable condensation could be attained without much dehydration. Comparing runs 3 to 8, it is seen that potassium and rubidium salts are equally effective while the sodium is less so. Calcium butyrate produced little condensation and curiously the octanol fraction boiled about 10° lower than with the other salts. In run 11 there was excessive dehydration, due to the high temperature. Runs 12 to 14 show that a much larger amount of the catalytic salt produces a good yield of octanol with little dehydration. In run 13 the tube was known to have leaked; the octanol represented a yield of 40% calculated on the recovered oil. A seven-hour run at 350° of propyl alcohol with 25% of potassium propionate gave 10% condensation. The efficiency of potassium salts may be due to their greater solubility.

Experimental

The caustic oxidations runs were made in a 3-in. (8-cm.) outside diameter chrome–vanadium steel tube of 800-cc. capacity. This was rocked through a small angle. It was electrically heated and the temperature was taken with a thermocouple. The condensation runs were made in a larger tube of the same kind. The charge was 1000 g. of dry butanol. Water was added to the reaction product to dissolve the salts and the oily layer separated, dried and fractionated.

Summary

1. A primary alcohol heated with sodium or potassium hydroxide is converted into the corresponding fatty acid salt; the alkali is used up completely if the alcohol is in excess.

2. The presence of water is advantageous; it prevents condensation of the alcohol with itself and darkening of the product.

3. Potassium and sodium salts of fatty acids are efficient catalysts for condensing two molecules of an alcohol into one of a higher.

The Action of Aluminum Chloride on Aromatic Hydrocarbons. I.[1] The 1,3-Dimethyl-4-butylbenzenes

BY DOROTHY NIGHTINGALE[2] AND LEE IRVIN SMITH

Anhydrous aluminum chloride brings about the migration of alkyl groups in aromatic hydrocarbons. Baddeley and Kenner[3] reported that when 1,3,4-tri-n-propylbenzene was warmed with aluminum chloride at 100°, the 1,3,5-tri-n-propyl isomer was formed, along with the lower and higher alkylated benzenes. They state that there can be little doubt that the normal character of the migrating propyl group was preserved, but offer no experimental proof for this statement. Smith and Perry[4] found that 1,3-dimethyl-4-t-butylbenzene warmed with aluminum chloride gave a 45% yield of the 1,3,5-isomer.

To study further the effect of aluminum chloride on 1,3,4-hydrocarbons, and to determine whether or not there is isomerization of the migrating radical, the four 1,3-dimethyl-4-butylbenzenes were chosen for this investigation.

It is well known that aluminum chloride and other metal halides cause isomerization of the alkyl radical, especially if the alkyl halide is primary. Shoesmith and McGechen[5] made a careful study of the reaction between the butyl halides and toluene and found that n-butyl chloride gave a 75% yield of m-s-butyltoluene and 25% of the p-isomer, rather than an o–p mixture. With isobutyl bromide, the $m:p$ ratio of t-butyltoluenes was 70:30.

In the syntheses of trialkylbenzenes from benzene or from m-dialkylbenzenes, by procedures involving the use of aluminum chloride as a catalyst, the principal product has the 1,3,5-configuration rather than 1,3,4- as would be expected. In

(1) Polymethylbenzenes. XXII. Paper XXI, THIS JOURNAL, 60, 652 (1938).

(2) Honorary Fellow, 1938. Present address: Department of Chemistry, University of Missouri, Columbia, Missouri.

(3) Baddeley and Kenner, J. Chem. Soc., 303 (1935).

(4) Moyle and Smith, J. Org. Chem., 2, 114 (1937).

(5) Shoesmith and McGechen, J. Chem. Soc., 2231 (1930).