OXIDATION of BUTYRIC ACID

WITH

CHROMIC ANHYDRIDE and SULFURIC ACID

Thesis

by

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In partial fulfillment of the requirements

for the degree of Bachelor of Science

in Chemical Engineering.

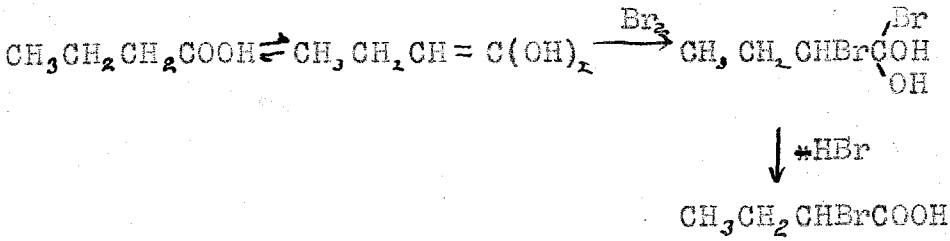
CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1924

I Introduction

When fatty acids are halogenated, alpha derivatives are the main product. According to the electronic displacement theory they should be the least formed. So, it is customary to believe that an enol form of the acid exists and that the bromine reacts with the enol form.



But the extremely slow oxidations of the acetate solutions indicate that there is no enolization under such conditions. However, such an enolization is possible in strong acid solutions if one or both of the hydroxyl groups of the enol form function as alcoholic hydroxyl.

This can be determined by studying the oxidation products of the fatty acids in strong sulfuric acid solution, using insufficient oxidizing agent for complete combustion.

If an enol form exists, then the propionic acid should be obtained from butyric acid.

/ Evans & Hines, J.A.C.S. 44,1543--6

$$CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH_2CH=C(OH)_2 \xrightarrow{2O} CH_3CH_2\underset{H}{\overset{O}{C}}=O + \underset{O}{\overset{OH}{C}}OH$$

$$\downarrow O$$

$$CH_2CH_2COOH$$

Three atoms of oxygen are used and there are produced 1 mol of CO_2 and 1 mol of H_2O in addition to the 1 mol of Propionic.

If an enol form does not exist, the other possibilities in the reaction mixture are

1. $CH_3CH_2CH_2COOH \xrightarrow{5\,O} CH_3COOH + (COOH)_2 + H_2O$

$$\downarrow H_2SO_4$$

$$CH_3COOH + CO + CO_2 + H_2O$$

Total result: 5O used, 1 mol CO and 1 mol CO_2 produce

2. $CH_3CH_2CH_2COOH \xrightarrow{6O} CH_2(COOH)_2 + CO_2 + 2H_2O$

$$\downarrow H_2SO_4 + \text{Heat}$$

$$CO_2 + CH_3COOH$$

Total result: 6O used; 2 mol CO_2 produced and 1 mol acetic.

3. $CH_3CH_2CH_2COOH \xrightarrow{3O} (CH_2COOH)_2 + H_2O$

$$\downarrow H_2SO_4 + \text{Heat}$$

$$CH_2\underset{CH_2}{\overset{CO}{\diagdown O \diagup}}CO + H_2O$$

Total result: 3O used; 1 mol succinic anhydride and 2 mol H_2O formed.

II Method of Attack

It was decided partially to oxidize a quantity of Butyric acid by the use ofChromic anhydride and seventy-three percent sulfuric acid. The gas evolved during the reaction was measured and analyzed for carbon dioxide and carbon monoxide and the oxidation mixture was steam distilled to separate the fatty acids resulting from the oxidation. The mixture of fatty acids was analyzed by converting them to their methyl esters and fractionating this mixture. From the weights of the various methyl esters formed, one may calculate the quantities of the various fatty acids arising from an incomplete oxidation of Butyric acid.

III Discussion of Experiment

The preliminary experiments consisted of finding a method of analyzing a mixture of Acetic, Propionic and Butyric acids. The methods tried were (1), Fractionation of aqueous mixtures of these acids, (2). Fractionation of a mixture of the anhydrous acids, (3) Separating the Propionic and Butyric acids from Acetic acid by saturating the aqueous mixture with calcium chloride, (4) Converting the acids to their sodium salts, esterfying these with dimethyl sulfate and fractionating the mixture of the esters.

The first three methods failed to give reliable results, as explained in detail in the latter part of this paper, but the fourth method gave results which checked very satisfactorily.

Butyric acid wasoxidized, using chromic anhydride and 73% H_2SO_4 and the gas evolved during the reaction was analyzed, for the gas analysis indicates in a way just how the reaction has gone (see Part 4) The mixture of fatty acids resulting from the oxidation were separated quantitatively from the oxidizing flask by steam distillation. Sodium carbonate was added directly to the steam distillate until it gave a neutral reaction to litmus and the whole was evaporated to dryness, powdered finely, and allowed to stand over night with 1 mol dimethyl sulfate. This method of preparing esters gives a yield of about 97%. A fractionation of methyl esters was carried out and a good separation resulted, as there is, roughly, twenty degrees between the boiling points of the successive esters.

Care should be taken in neutralizing the fatty acids in the steam distillation for an excess of sodium carbonate will react with the dimethyl sulfate and form dimethyl carbonate, B.P. 89.7°, which will cause an error in the calculation of the weights of the esters prepared.

IV Conclusions

As the quantity of iso Butryic acid is small in comparison to the quantityy of normal butyric acid, the mechanism of the reactions can be arrived at by simply studying the possible reactions of normal Butyric acid.

If the enol form of the acid exists in concentrated acid solutions, then the oxidation should progress successively down the chain; that is, Propionic acid should be one of the oxidation products of Butyric acid and Acetic acid should be the oxidation product of Propionic acid. Under these conditions one may set up the equation involving the gas analysis and the analysis of the esters from the steam distillate,

mols carbon dioxide formed = mols propionic acid + 2(mols acetic acid)

From the gas analysis the mols of carbon dioxide evolved were found to be .19 mol. The analysis of the methyl esters resulting from the oxidation indicate 0.0320 mol propionic acid and 0.0744 mol acetic acid. Substituting in the equation, one gets

$$.19 = .032 + 2 \times .0744$$

or $$.19 = .18$$

which is well within the limit of the experimental error.

There is also another equality in this reaction which can be shown in the form of an equation, that is, as three atoms of oxygen are used to oxidize one mol of Butyric acid forming Propionic acid, carbon dioxide and water, two-thirds of the available oxygen goes to forming carbon dioxide. Hence,

mols $CO_2 = \frac{2}{3}$ Mols available oxygen.

The reaction by which the oxygen is formed is essentially

$$2\ CrO_3 = Cr_2\ O_3 + 3O$$

and when only one half mol of chromic anhydried is used in the oxidation, there will be available only .375 mol oxygen. The last equation then becomes

$$.19 = \frac{2}{3} \times .375$$

or $.19 = .25$

The evaluation of the equation shows that about twenty-five percent of the available oxygen is unaccounted for when complete reduction of the chromic anhydride is assumed. The analysis of the methyl esters resulting from the steam distillation accounts for all of the original Butyric acid so it is concluded that the reduction of the chromic anhydride was not quantitative under the conditions of this experiment.

Referring to the equations in the introduction, the oxidation could not have proceeded according to equation (1) for that reaction requires carbon monoxide to

be produced and no propionic acid to be formed. No trace of carbon monoxide was found in the gases evolved during the oxidation and propionic acid was formed by oxidation.

The reaction could not have proceeded according to equation (2) for thisreaction produces no propionic acid. Equation (3) is also ruled out on two counts, first, that no propionic acid would result by thisreaction and second, that no carbon dioxide would be formed according to this reaction, both of these requisites are decidedly contrary to the experimental results.

As all the experimental data point to the oxidation thru the enol form of the acid and eliminates any other mechanism for the reaction, it is concluded that the enol form does exist in strong acid solution, and if any part of the oxidyzing agent is used up as indicated by equations (1), (2) or (3), that part is so small that the products escape detection by this method of analysis.

V Experiments in Detail

The preliminary experiments consisted in finding a method of analyzing a mixture of Butyric, Propionic and Acetic acids. The first attempt was to fractionate an aqueous mixture of known composition of these three

acids, using a 24 inch Hempel fractionating column filled with beads.

The first portion of the distillate, which came over at 99°, tested strongly acid, so this method of separation was discontinued. These fatty acids have abnormal vapor pressures[1] in aqueous solutions and cannot be separated by fractionation from an aqueous mixture.

A similar fractionation was carried out using anhydrous acids prepared by treating the dry sodium salts of the fatty acids with 100% H_2SO_4 but the same difficulty was encountered. The anhydrous acids absorbed water from the atmosphere during the fractionation and again exhibited abnormal vapor pressures.

If an aqueous mixture of Butyric, Propionic, Acetic and Formic acids is saturated with calcium chloride, Butyric and Propionic acids will form a separate oily layer and Acetic and Formic acids will remain in the lower layers.[2]

If the two layers are separated and then each is separately titrated with standard $Ba(OH)_2$ and the weight of precipitate determined, then the weight of each of the constituents may be calculated.

A known mixture of Butyric acid and Propionic acid

1 Witzemann; J.A.C.S. 41, 1946- 1951
2 Commercial Organic Analysis--Allen I 487

containing about 90% water (which is comparable to that obtained by steam distillation) was saturated with calcium chloride but the experiment failed to give two layers.

If dry Potassium acetate is distilled with 1⅓ mol dimethyl sulfate a quantitative yield of methyl acetate is produced.[1]

A mixture of 3.0 gm. Sodium acetate, 26.9 gm. Sodium Propionate and 20.05 gm. Sodium Butyrate was distilled with 84 gm. dimethyl sulfate, and the various fractions of the distillate were caught in weighed bottles and refractionated until a good separation was obtained.

First Fractionation		Fifth Fractionation	
Fraction	Weight	Fraction	Weight
- -63°	1.8	-- 63°	0.7
63---70°	1.7	63--70°	1.4
70---76°	2.6	70--76°	1.4
76---85°	13.5	76--85°	14.2
85---95°	9.9	85--95°	3.6
95--109°	11.3	95-109°	13.9
Total	40.8	Total	35.2

If the weights of the intermediate products are divided equally between the esters lying on either side of the intermediate fraction, and their weights be multiplied by the ratio of $\frac{40.8}{35.2}$, one obtains:

1. C.Graebe, Annalen Der Chemie , 340, 247

mols Acetate	.040
mols Propionate	.283
mols Butyrate	.203
Total	.526

While in the original mixture there were:

mols Acetate	.036
mols Propionate	.280
mols Butyrate	.182
Total	.498

Thus, the fatty acids in the oxidation mixture could calculated to within five percent accuracy.

Oxidation Experiment

The Butyric acid used in the oxidation was obtained by fractionating " Finch Refined Butyric Acid" twice, collecting that portion of the distillate which came over between 160° and 165° corrected. The amount obtained was about one-fifth of the original volume. Apparatus used consisted of a three liter balloon flask equipped with a side arm which led to an aspirator for the purpose of collecting the gases evolved during the reaction. The mouth of the balloon was fitted with a two-holed stopper carrying a mercury sealed stirrer and a tube thru which 75% sulfuric acid could be admitted.

Half a mol of Butyric acid (44gm.) and half a mol of chromic anhydride (50 gm.--enough to oxidize one-fourth mol of Butyric acid to Propionic acid and car-

bonic acid) were placed in the balloon and the agitation was started. No evolution of gas took place until about 25 c.c. of the sulfuric acid had been added; the reaction mixture, which had been cooled to prevent the temperature from going above 50°, gave off no more gas and the reaction had gone to completion. The volume of water displaced by the gas was measured and corrected, and a gas analysis of the gases in the aspirator and in the balloon flask was made.

It was found that 1300 c.c. CO_2 had been given off and that there was no CO present.

Steam Distillation of Oxidation Mixture

The steam distillation was carried on using this same balloon flask with a condenser attached to the side arm. Steam at 100° was used. After one liter of distillate had been collected, the condensate tested neutral.

The sodium salts of the acids were next prepared by neutralizing the steam distillate with Na_2CO_3 until the solution was neutral to litmus. The sodium salts were dried for one hour at 110°, finely powdered, and allowed to stand over night with 88 grams of $(CH_3)_2 SO_4$ in an ordinary round-bottomed flask equipped with a Hempel fractionating column.

The fractionation was carried out in the same manner

as was the fractionation of the methyl esters in the preliminary experiment. After five fractionations there resulted:

Fraction	Weight	
--60°	1.45 gm	.019 mol
76°--85°	.80 gm	.010 mol
95°--109°	21.60 gm	.212 mol
	Total	.241 mol

This quantity is just half of what should have been the yield, as ½ mol of Butyric was used in the oxidation.

During the experiment a quantity of mercury leaked from the mercury seal of the stirring device into the reacting mixture and reduced some of the H_2SO_4 to SO_2. It is believed that this SO_2 used up some of the oxidation agent in being oxidized to SO_3 and thus hindered the oxidizing agent from reacting solely with the fatty acids.

The oxidation experiment was repeated, using the same quantities of materials as before, taking care that no mercury leaked into the reacting mixture. From the gas analysis it was found that there were .19 mol of CO_2 evolved, and that no CO was evolved.

The analysis of the esters is given below.

First Fractionation		Fifth Fractionation	
Fraction	Weight	Fraction	Weight
-- 63°	3.55	63°	3.65
63°--70°	1.93	63°-70°	.63
70°--76°	.93	70°--76°	.23
76°--85°	1.90	76°--84°	1.20
85°--95°	3.75	84°--89°	.90
95°-109°	26.30	89°--95°	2.30
109°--	9.20	95°--99°	1.70
		99°-106°	24.70
Total	47.56	Total	35.31

After correcting the weights of the various fractions as previously indicated, one obtains

Methyl Acetate	5.50 gm.	.0744 mol
Methyl Propionate	2.81 gm	.0320 mol
Methyl iso Butyrate	4.85 gm	.0475 mol
Methyl Butyrate	34.40 gm	.3380 mol
Total		.4919 mol

From these results it may be calculated that there were in the oxidation mixture resulting from the oxidation of 44gm, one half mol Butyric acid.

Acetic Acid	4.46 gm	.0744 mol
Propionic Acid	2.36 gm	.0320 mol
Iso Butyric Acid	4.18 gm	.0475 mol
Butyric Acid	29.60 gm	.3380 mol
Total		.4919 mol

During the latter part of the fractionation it was observed that a large part of the fraction from 85°-95° came over around 92°, which would not have been the case had there been only Methyl Propionate and Methyl Butyrate present. The fraction was split up into two parts

84-89° and 89-95°, and a much better fractionation was obtained. As this fraction had a boiling point of 92°, it was concluded that it consisted of Methyl iso Butyrate and also that the original Butyric acid had some Butyric acid in it.

The original Butyric acid was analyzed by converting to methyl esters, and these were fractionated four times. It was found that from 37 gm. (.43 mol) there were obtained 4.53 gm. Methyl iso Butyrate and 30.0 gm. Methyl Butyrate; from which it can be calculated that there was 10.2% iso Butyric acid in the original Butyric Acid. In the methyl esters resulting from the oxidation experiment, the percentage of the iso Butyric Acid undergoes oxidation a little more readily than the normal Butyric Acid.

SUMMARY

1. A method of quantitatively separating moderately large quantities of fatty acids has been developed. The method, which has an accuracy of about five per cent, consists in converting the sodium salts into the methyl esters and separating these by fractional distillation.

2. Butyric acid was oxidized by means of chromic anhydride in the presence of seventy three per cent sulfuric acid.

3. No carbon monoxide was formed.

4. Propionic and acetic acids were formed.

5. The number of mols of carbon dioxide formed were equal to the number of mols of propionic acid plus twice the number of mols of acetic acid formed.

6. The number of mols of propionic and acetic acids plus the number of mols of unoxidized butyric acid equaled the number of mols of original butyric acid.

7. It was concluded that oxidation of butyric acid by means of chromic anhydride and sulfuric acid takes place through the enol form of the acid, and progresses successively down the chain.