THE HYDROLYSIS OF AROMATIC SULPHONIC ACIDS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED The Hydrolysis of Aromatic Sulphonic Acids.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry.

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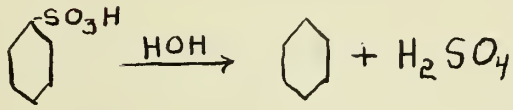
The Hydrolysis of the Aromatic Sulphonic Acids.

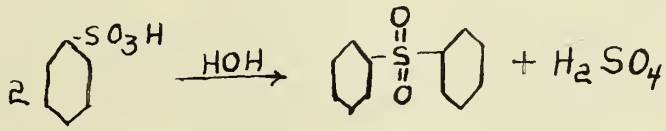
I. Introduction

Altho the problem of hydrolyzing aromatic sulphonic acids to the hydrocarbons is not a new one, nevertheless, it has never been studied in a systematic manner. The author's work was mainly to study the effect of the number of groups in the ring, position, kind of groups and catalyzers on the amount and rate of hydrolysis. Along the same line of work the various temperatures of hydrolysis were determined which suggests the possibility of a separation of various aromatic compounds by fractional hydrolysis of their sulphonic acids.

II History.

Freund (1) in 1861 found that on dry distilling benzene sulphonic acid he obtained a product that had a strong odor and a large refractive index. This compound he called benzene. He believed either one of two things happened.

I 

II 

Later in 1865 Beilstien (2) used a method of dry distillation for the recovery of xylene from its sulphonic acid and later in 1878 Jacobson (3) used a similar method to recover metaxylene from its sulphonic acid.

Armstrong (4) in 1878 separated mesitylene and pseudocumene by heating their sulphonic acids at 100° with muriatic acid whereby the mesitylene sulphonic acid is alone hydrolyzed; the pseudomene is recovered by heating at 130° - 140°. It was long known that mesitylene could be separated from its sulphonic acid by mere steam distillation. The same author in 1883 applied these methods to the tetra-methyl benzenes.

Miller and Armstrong (5) did the first real work on the subject and used the method that was used in this work. The method consisted in passing the steam thru a hot

concentrated acid solution until hydrolysis takes place. They stated that the rate of hydrolysis does not depend on the excess of sulphuric acid but that the sulphuric acid is necessary to obtain a high temperature. They experienced no difficulty in separating calcium and barium salts by their methods. They stated that the sources of error are:

(a) Thru dissolution of a small quantity in water.

(b) Thru incomplete separation of hydrocarbon.

(c) Thru evaporation of hydrocarbon.

They tabulated the hydrolysis points of benzene, toluene, ortho, meta and paraxylenes sulphonic acids, etc., and suggested the possibility of separating various hydrocarbons by fractional hydrolysis of their sulphonic acids but state that this is almost impossible because hydrolysis is generally carried out at a temperature higher than the critical hydrolysis temperature. They also did considerable work with the hydrolysis of sulphonic acids in sealed tubes and found that the temperatures of hydrolysis were very different under these conditions.

Kelbe (6) in 1886 improved the Miller and Armstrong method somewhat by passing steam thru a heated copper tube before passing it thru the solution. The advantages are that a large excess of sulphuric acid is avoided and also that ortho brom toluene and ortho brom xylene prepared by this method seemed to be more stable toward oxidizing agents than those prepared by other methods.

Jacobson (7) in 1887 found that when sodium pentamethylbenzenesulphonate is shaken with concentrated sulphuric acid and light petroleum, hydrolysis occurs and the hydrocarbon is obtained on evaporation showing the effect of a number of groups in the ring on hydrolysis.

Later Friedel and Craft (8) used aluminum chloride and phosphoric acid to bring about the hydrolysis of the aromatic sulphonic acids and obtained good results; the yields in the relatively few cases tried were greater than those with sulphuric acid. In the present work it was found that almost invariably with phosphoric acid the yield is about the same or greater than the yield with sulphuric acid as a catalyst.

Fournier (9) in 1892 used Friedel and Craft methods to obtain diethyl benzene from diethyl benzene sulphonic acid with almost theoretical results.

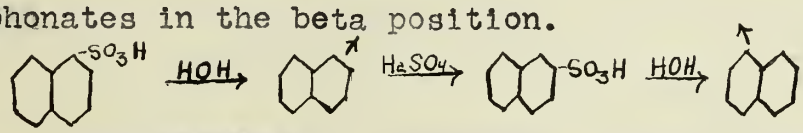
Later in 1901 J.M. Craft (10) studied the rate of hydrolysis of sulphonates; chiefly metaxylene sulphonate for 10 - 35% of hydrochloric acid heated in sealed tubes at 100°. The amount of hydrolysis was noted for different amounts of hydrochloric acid and the velocity of reaction was found to be proportional to the concentration of the catalytic agent. With an increase of 6% in concentration there is a velocity four times as great. Craft does not fully understand the reason for this phenomena.

III Theoretical.

Most of the previous writers have mentioned the fact that benzene sulphonic acid can be hydrolyzed almost quantitatively but these results could not be duplicated.

When we introduce an (OH) group in the benzene ring the ortho and para hydrogens are greatly activated and hydrolysis seems to take place easier. Thus para phenol sulphonic acid hydrolyzes very easily; the rate being greater with phosphoric acid as a catalyzer than with sulphuric acid as a catalyzer.

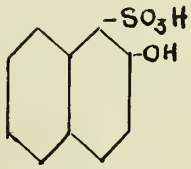
They yield of napthalene from alpha and beta napthalene sulphonic acids are almost theoretical using sulphuric acid as a catalyzer. With phosphoric acid as a catalyzer the rate of hydrolysis is faster and the yield is about the same. The alpha napthalene sulphonic acid comes over rapidly at first and suddenly stops which seems to indicate that the sulphonic acid group is split off and resulphonates in the beta position.



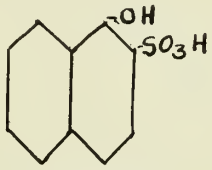
The yield with phosphoric acid is greater with the alpha than with the beta napthalene sulphonic acid.

When the (OH) group is introduced into the napthalene rings in the beta position the hydrolysis is decreased. Bender (11) found a method of preparing napthol (1) sulphonic acid (2) and stated that it hydrolyzed readily with sulphuric

acid with theoretical results. From this we would believe that when the sulphonic acid group is in the alpha position it splits off and rearranges itself in the beta position before hydrolyzing. This is almost impossible because of the fact that the (OH) group is in the beta position and therefore the hydrolysis would be low. In the case where the sulphonic acid group is in the beta position hydrolysis is rapid.



Naphthol (2) Sulphonic Acid (1)



Naphthol (1) Sulphonic Acid (2)

The amount of hydrolsis of napthol (2) sulphonic acid (1) with sulphuric acid and phosphoric acid as catalyzers is about the same.

The ortho, meta and para toluene sulphonic acids were then studied in order to give us an idea as to the effect of position in the ring relative to the time and amount of hydrolysis. With sulphuric acid as a catalyzer we found that the ortho toluene sulphonic acid hydrolyzes and that the meta and para toluene sulphonic acids do not showing that position in the ring does have an effect. With phosphoric acid as a catalyzer we found that the para toluene sulphonic acid hydrolyzes easier than the ortho toluene sulphonic acid so we can see that the catalyzer has an effect on the rate of hydrolysis as well as the position of the ring has an effect on the rate of hydrolysis. If conclusions are to be drawn from a series of experiments of

this nature the same catalyzers must be used through out.

The para chloro, para bromo and para iodo benzene sulphonic acids were next studied with a view of seeing whether or not the weight of the group in the ring had anything to do with the amount and time of hydrolysis. With sulphuric acid as a catalyzer we have for chloro benzene sulphonic acid 12% hydrolysis, for bromo benzene sulphonic acid 37% hydrolysis and for iodo benzene sulphonic acid 56% hydrolysis showing that as the molecular weight increases the amount of hydrolysis increases. With phosphoric acid as a catalyzer this is also true but the rate and amount of hydrolysis are considerably greater. In the case of chloro benzene sulphonic acid the hydrolysis is just four times as great and the time of hydrolysis is shorter. In each case phosphoric acid is a better catalyzer of the two. This may be because with an excess of sulphuric acid there is a greater tendency to resulphonate. In all the cases mentioned we can see that the kind of group has an effect on hydrolysis and also that with increasing molecular weight the amount is greater.

The sodium meta nitro benzene sulphonate was found to act very differently from other sulphonates studied. The distillate from the hydrolysis with sulphuric acid was of a yellow color and the residue in the flask was mainly carbon showing that the molecule was destroyed. The distillate contained no nitro benzene and did not give a test for nitric acid. Phosphoric acid was tried with no better results.

Evidently the nitro compounds decompose very differently from the other sulphonic acids studied.

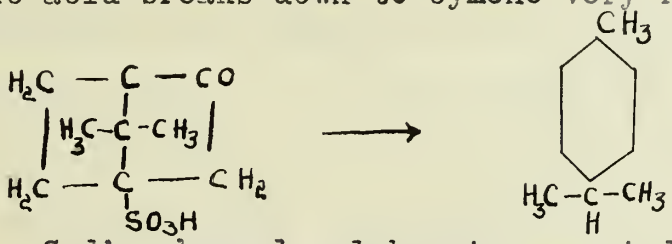
Jacobson (7) found that the penta methyl benzene sulphonic acid decomposed on mere shaking with sulphuric acid. With these facts in mind it was thought that increasing the weight of an aliphatic side chain might have an analogous effect. With these compounds however the increase of hydrolysis does not exactly follow the rule. We notice that the para toluene sulphonic acid does not hydrolyze with sulphuric acid as a catalyzer. The ethyl benzene and secondary butyl benzene sulphonic acids do hydrolyze showing that an increase in the weight of the molecule increases the amount of hydrolysis. With the use of phosphoric acid as a catalyzer the yields are practically doubled showing that phosphoric acid is a better catalyzer.

With lauryl benzene sulphonic acid the heat generated by the addition of sulphuric acid to the water solution was sufficient to hydrolyze the sulphonic acid. We can see from this the effect of the weight of the group or groups in the ring on the amount and time of hydrolysis. Sodium para chloro benzene sulphonate was then hydrolyzed and the introduction of another group in the ring had a marked effect on the amount of hydrolysis, the hydrolysis with both sulphuric acid and phosphoric acid as catalyzers being about 80%.

With the use of sodium ortho dichloro benzene sulphonate we have a similar reaction, the hydrolysis with

sulphuric acid being about 65%. In this case the hydrolysis with sulphuric acid is greater than with phosphoric acid as a catalyzer. Similarly with ortho xylene sulphonic acid we have the same effect of additional groups in the ring although the yield is not the same as the yield with the sodium ortho dichloro benzene sulphonate.

It has long been known that camphor when steam distilled in the presence of a dehydrating agent gave cymene. It was found that in a similar manner camphor sulphonic acid breaks down to cymene very readily.



Sodium benzyl sulphonate was studied to see what effect hydrolysis would have on an aliphatic hydrocarbon in comparison with an aromatic hydrocarbon. Sulphuric acid and phosphoric acid were both used as catalyzers but with negative results.

In the preparation of lauryl benzene by the Friedel and Craft reaction an intermediate compound perhaps dodecylene, was isolated. It gave the bromine test for unsaturation and its boiling point and specific gravity was like that of dodecylene. This may be evidence in favor of the theory that the first steps in the ordinary Friedel and Craft reaction is a splitting out of the halogen acid from the alkyl halide.

IV. Experimental.

Apparatus.

The apparatus used was a simple steam distillation apparatus. The distilling flask was connected to an air condenser which in turn was connected to a water condenser. All the connections leading into the flask were made of pyrex tubing and because of the high temperatures of hydrolysis the thermometer was incased in a pyrex tube which was filled with cotton seed oil. This precaution was taken to prevent the thermometer from being broken and to prevent the numbers on the thermometer from being effaced.

Preparation of Compounds.

The following compounds were already prepared and therefore there is no need of discussing their methods of preparation: sodium benzene sulphonate, sodium beta napthalene sulphonate, sodium para brom benzene sulphonate, sodium meta nitro benzene sulphonate, sodium para chlor toluene sulphonate, sodium ortho dichloro benzene sulphonate, sodium ortho xylene sulphonate, methyl ether of carvocrol sulphonic acid and camphor sulphonic acid.

Sodium alpha napthalene sulphonate:- This compound was prepared according to the method of Barnett (12) which will not be described here. It was found that when the alpha napthalene sulphonic acid was boiled with water

to remove the napthalene that a considerable amount was hydrolyzed and it was almost impossible to obtain a product uncontaminated with napthalene. Sodium carbonate was added to the solution and it was found that the sodium salt was relatively stable to boiling with water so that in this manner the compound could be easily purified.

Para phenol sulphonic acid:- This compound was prepared according to Vanino (21). Two hundred (200) grams of phenol was melted at 35° - 40°, 100 grams of fuming sulphuric acid was added care being taken that the temperature does not rise too high. This mixture was heated slightly and allowed to stand for about twenty-four hours. The two layers gradually disappeared and on standing the sulphonic acid crystallised out. The slight excess of sulphuric acid was not removed because it was not necessary for the experiment.

Sodium napthol (2) sulphonate (1):- To about 40 grams of b-napthol about 100 c.c. of sulphuric acid (mixture of 7% fuming sulphuric acid and concentrated sulphuric acid) was added and the whole mass heated on an oil bath to 160° until the two layers disappeared. The excessof sulphuric acid was neutralized with barium hydroxide, the barium sulphate filtered off and the filtrate added to a saturated sodium chloride solution. The yield was poor, about 9 grams.

Sodium ortho toluene sulphonate:- Several methods were tried in the preparation of sodium ortho toluene sul-

phonate. The amide of o-toluene sulphonic acid was refluxed for several hours with a sodium carbonate solution but with little success.

The method of hydrolysis described in Winther (13) which uses chlorsulphonic acid was tried. This method consists in heating the amide with chlorsulphonic acid for several hours at 130° - 150°, extracting with ether and hydrolyzing with sodium carbonate. The reaction did not work.

Finally a mixture of ortho and para toluene sulphonyl chlorides were separated by vacuum distillation as used by Majert and Ebers (14). About thirty parts in a hundred were distilled over giving us the ortho compound and by a series of vacuum distillations the ortho compound was obtained pure. This sulphonyl chloride was hydrolyzed by refluxing with a saturated sodium carbonate solution with almost theoretical results.

Sodium meta toluene sulphonate:- This compound was prepared according to the method of Metcalf (15) and Griffin (16). To 100 grams of para toluidine was added 200 grams of 7% fuming sulphuric acid. This mass was heated until fumes of sulphur dioxide came off and the mixture kept at 180° for an hour. After cooling the mixture was poured into twice its volume of water and a dark pasty mass resulted consisting mainly of the meta and ortho sulphonic acids of para toluidine. The remaining sulphuric acid was precipitated by an excess of barium hydroxide, the solution boiled to remove any unchanged toluidine and

the barium sulphate filtered off. On cooling the long sulphur yellow needles crystallized out. This was filtered off and the ortho and meta sulphonic acids were separated by difference of solubility ina potassium hydroxide solution. The para toluidine meta sulphonic acid is insoluble while the para toluidine ortho sulphonic acid is soluble in the potassium hydroxide solution.

Twenty-five (25) grams of the potassium para toluidine meta sulphonate was suspended in a 150 c.c. of a 92% solution of alcohol to which hydrochloric acid had been added. This was placedin an ice bath and when the temperature was at 0° sodium nitrite was added and the temperature gradually allowed to rise up to 46° until the reaction was complete, which requires about 30 minutes. The pinkish white crystals were filtered off by a filter pump and washed with alcohol.

Twenty (20) grams of this diazo compound was decomposed in 200 c.c. of absolute methyl alcohol to which 9 grams of dried sodium carbonate had been added. This reaction was carried on at 0° and the solution gradually warmed to 30°. This solution was allowed to stand over night and then heated to 35°. The alcohol was distilled off and the resulting mixture was so contaminated with sodium chloride that it was almost impossible to obtain a pure product.

Instead of sodium nitrite, amyl nitrite was used with better results, because a sodium salt was not formed.

This method is practically the same except that the diazo compound was prepared and decomposed in the same alcoholic suspension. The yield was poor, from about 25 grams of the potassium para toluidine meta sulphonate only 6 grams of the dark impure potassium meta toluene sulphonate resulted.

Sodium para toluene sulphonate:- This compound was prepared by refluxing para toluene sulphonyl chloride with a saturated sodium carbonate solution for about an hour. The reaction goes very easily and the yield is almost quantitative.

Sodium para chlor benzene sulphonate:- This compound was prepared by the same method as used by Langmuir (17) in preparing sodium para iodo benzene sulphonate. 60 c.c. of chlor benzene was heated with 120 c.c. of an equal mixture of 7% fuming sulphuric acid and concentrated sulphuric acid on an oil bath for several hours or until the two layers had disappeared. This solution was added to the same amount of water and finally when cooled poured into a saturated sodium chloride solution. The sodium para chlor benzene sulphonate was filtered off by suction. The yield was good, about 70 grams.

Sodium para iodo benzene sulphonate:- This compound was prepared by the previous mentioned method of Langmuir. From 50 grams of iodo benzene, 35 grams of the sodium para iodo benzene sulphonate was obtained.

Sodium para ethyl benzene sulphonate:- To 50 c.c. of ethyl benzene 100 c.c. of a mixture of 7% fuming sulphuric

acid and concentrated sulphuric acid was added and the mixture heated gently on a steam cone until the two layers mixed; allowed to stand several hours and added to 100 c.c. of water. The excess of acid was neutralized with sodium carbonate and then the mass was added to a saturated sodium chloride solution. The sodium salt crystallized out in beautiful leaflets; yield about 35 grams.

Secondary Butyl benzene:- Two runs were made in the preparation of this compound. In the first run 45 c.c. of normal butyl bromide and 140 c.c. of benzene were dried over calcium chloride and then refluxed with 20 grams of aluminum chloride for about three-fourths of an hour. The mass was then poured into water. The two layers were separated and the benzene extraction dried over calcium chloride for about four hours. The benzene was distilled off and the remainder was fractionated; the fraction boiling at 172° - 176° at atmospheric pressure. The yield was 34 grams.

In the second run 50 c.c. of normal butyl bromide, 200 c.c. of benzene and 20 grams of aluminum chloride were used. The yield was 35 grams.

This reaction according to Schram (18) who used normal butyl chloride instead of normal butyl bromide gives the secondary butyl benzene. The boiling point of the compound (173° - 175°) and the specific gravity (0.865) found, corresponded to that for secondary butyl benzene.

Sodium secondary butyl benzene sulphonate:-

34 grams of secondary butyl benzene, 50 c.c. of concentrated sulphuric acid and 20 c.c. of 7% fuming sulphuric acid were allowed to stand for several hours in the cold but there was no reaction. The mass was then heated on a steam cone for several hours until the two layers disappeared. The excess of acid was neutralized with sodium carbonate and the resulting mixture added to a saturated sodium chloride solution. The yield of the sodium salt was 15 grams.

Lauryl bromide:- This compound was prepared according to the method of Kamm and Marvel (19). In a 250 c.c. round bottom flask 40 grams of lauryl alcohol, 85 grams of hydrobromic acid (34%) and 42 c.c. of sulphuric acid were refluxed for about three hours. The solution was diluted with water, the bromide separated by difference of specific gravities and then washed with sulphuric acid, water and dilute sodium carbonate solution successively. The bromide was extracted with ether. The ether was then evaporated off and the product distilled under a vacuum of about 40 mm., the bromide coming over at 196° - 200°. The yield was 30 grams or about 55% of the theory. Undoubtedly the low yield is due to the fact that a 34% solution of hydrobromic acid was used while the directions call for a 48% solution.

Lauryl benzene:- The reaction of Friedel and Craft was used in the preparation of this compound. 29 grams of lauryl bromide, 250 c.c. of benzene and 25 grams of aluminum chloride were refluxed for four hours. The

resulting solution was poured into water and the two layers separated. The benzene layer was dried over calcium chloride over night, benzene was distilled off and the remainder distilled under a vacuum of 46 mm. Two fractions were collected, the boiling point of the first fraction was 100° - 110° and the yield was 8.50 grams, while the second was 190° - 197° and the yield was 10 grams. The first fraction is perhaps dodecylene because is gave a positive test for unsaturation and the specific gravity was almost that of dodecylene, while the second fraction is undoubtedly lauryl benzene. The specific gravity of lauryl benzene was found to be 0.9225 at 20° and its boiling point 190° - 197° at 46 mm. pressure. In odor and general appearance lauryl benzene resembles the higher aliphatic hydrocarbons.

Sodium lauryl benzene sulphonate:- To 7 grams of lauryl benzene 20 c.c. of concentrated sulphuric acid and 10 c.c. of 7% fuming sulphuric acid were added. This mixture was occasionally shaken and sulphonated very readily in the cold. It was poured in a similar amount of water, the excess of acid neutralized the sodium carbonate and finally added to a saturated sodium chloride solution where the sodium salt crystallized out. The yield was very poor; about 2 grams. This poor yield may be explained by the fact that hydrolysis took place when it was poured into water.

Sodium benzyl sulphonate:- The potassium salt of this compound was first prepared by Böhler (20), by

refluxing benzyl chloride with potassium sulfite. To 100 grams of benzyl chloride a solution containing 125 grams of sodium sulfite was added and this mixture refluxed for about five hours. When the reaction was finished there remained an oil which had a boiling point of 190° and is evidently benzyl alcohol. On cooling the solution the sodium benzyl sulphonate crystallized out in beautiful leaflets. The yield is 85 grams or about 45% of theory. The yield of benzyl alcohol was 40 c.c.

In figuring the yields in the following data the author in each case endeavoured to prepare the mono sulphonic acid and all the yields are figured approximately on this basis.

DATA

Name	Amt	Composition	Temp	Time	Yield	%
Sodium benzene sulphonate.	100 g.	250 c.c. H_2SO_4	115°	2 hrs	-	-
	100	" " "	190-200	2	-	-
	10	25 c.c. H_3PO_4	200-240	3/4	-	-
Para phenol sulphonic acid	20	25 c.c. H_2SO_4	180-200	1	6.5	60
	20	" " "	" "	1 1/6	7.0	65
	20	40 c.c. H_3PO_4	" "	2/3	9.5	88
Sodium beta napthalene sulphonate.	125	200 c.c. H_2SO_4	190-200	1	10.0	-
	20	75 " "	165-190	2	4.0	40
	25	" " "	175-195	3	7.5	60
	10	50 " "	160-170	2	2.25	45
	10	" " "	" "	"	"	"
	10	" " "	" "	3	4.5	90
	10	25 " H_3PO_4	160-200	1/2	3.25	65
Sodium Alpha napthalene sulphonate.	10	75 C.c. H_2SO_4	160-180	2	2.0	40
	10	25 " "	" "	1 1/2	2.0	40
	5	50 " H_3PO_4	170-210	25 min.	2.5	90
Sodium napthol(2) sulphonate(1).	9	25 c.c. H_2SO_4	140-160	1 1/4	1.5	26
	6.5	" " "	" "	3/4	1.25	30
Sodium ortho toluene sulphonate.	10	25 c.c. H_2SO_4	200-220	1/2	0.43	8
	10	34 " H_3PO_4	" "	1/2	1.07	19
Sodium meta toluene sulphonate.	6	25 c.c. H_2SO_4	160-180	1 1/4	-	-
Sodium para toluene sulphonate.	10	75 c.c. H_2SO_4	220-230	2	-	-
	10	" " "	" "	1 1/2	-	-
	10	" " "	" "	2	-	-
	10	25 " H_3PO_4	200-220	1/2	2.8	50
Sodium para chloro benzene sulphonate.	9	25 c.c. H_2SO_4	220-250	2/3	0.55	10
	10	" " "	" "	3/4	0.55	11
	10	" " H_3PO_4	" -310	1/2	2.2	48
Sodium para Iodo benzene sulphonate.	10	25 c.c. H_2SO_4	240-250	1/2	3.68	56
	10	50 "	" "	2/3	4.14	63
	10	25 " H_3PO_4	220-250	1/2	4.41	66
Sodium meta nitro benzene sulphonate.	10	25 c.c. H_2SO_4	200-220	1	-	-
	10	40 " H_3PO_4	" "	1	-	-
Sodium para ethyl benzene sulphonate	10	25 c.c. H_2SO_4	190-230	1/2	1.54	30
	10	" " "	" "	3/4	1.54	30
	10	30 " H_3PO_4	140-200	1	2.18	43
	10	50 " "	" "	3/4	2.18	43

DATA (Continued)

Sodium para secondary butyl benzene sulphonate.	5 10	50 c.c. H_2SO_4 " " H_3PO_4	170°-195° 170-210	1/3 1/2	0.64 2.58	23 47
Sodium lauryl benzene sulphonate.	Hydrolyzes almost quantitatively on addition of sulphuric acid.					
Sodium para chlor toluene sulphonate.	10 10 10	35 c.c. H_2SO_4 " " " H_3PO_4 50 "	200-220 " " " 240-280	1 1/6 " " 3/4	4.81 2.14 4.28	87 40 77
Sodium ortho dichloro benzene sulphonate	10 10 10	25 c.c. H_2SO_4 " " " " " H_3PO_4	240-280 " " 260-320	3/4 " 35 min.	4.00 " 3.30	66 " 55
Sodium ortho xylene sulphonate.	10 10	25 c.c. H_2SO_4 " " "	160-180 150-180	1 3/4	1.88 1.54	45 35
Methyl ether of carvocrol sulphonic acid.	10 6	25 c.c. H_2SO_4 " " "	160-170 " "	25 min. "	3.88 2.18	50 52
Camphor sulphonic acid.	10 10	25 c.c. H_2SO_4 50 " H_3PO_4	160-170 160-180	1/2 "	2.40 3.90	25 40
Sodium benzyl sulphonate.	10 10	25 c.c. H_2SO_4 40 " H_3PO_4	160-210 " "	1 "	- -	- -
Sodium para bromo benzene sulphonate.	10 10 10	25 c.c. H_2SO_4 25 " " " 25 c.c. H_3PO_4	200-210 200-240 220-240	1 1 1/4	2.98 3.72 4.10	45 57 62

V SUMMARY.

I The following compounds were prepared and the amount, time and temperatures of hydrolysis studied: Sodium benzene sulphonate, Para phenol sulphonic acid, Sodium beta napthalene sulphonate, Sodium alpha napthalene sulphonate, Sodium napthol (2) sulphonate (1), Sodium ortho toluene sulphonate, Sodium meta toluene sulphonate, Sodium para toluene sulphonate, Sodium para chloro benzene sulphonate, Sodium para bromo benzene sulphonate, Sodium para iodo benzene sulphonate, Sodium meta nitro benzene sulphonate, Sodium para ethyl benzene sulphonate, Sodium para secondary butyl benzene sulphonate, Sodium lauryl benzene sulphonate, Sodium para chlor toluene sulphonate, Sodium ortho dichloro benzene sulphonate, Sodium ortho xylene sulphonate, Methyl ether of carvocrol sulphonic acid, Camphor sulphonic acid, and Sodium benzyl sulphonate.

II It has been shown that the time and amount of hydrolysis of aromatic sulphonic acids depends on:

(a) Kind of groups in ring.

(b) Number of groups in ring.

(c) Position of groups in ring.

III Phosphoric acid was used as a catalyzer and in many cases was superior to sulphuric acid as a catalyzer.

IV Sodium benzyl sulphonate was found to act very differently from the other compounds studied showing the characteristics of the aliphatic compounds.

V Lauryl benzene has been prepared and its physical constants determined. It was shown that it sulphonates very readily but that the sulphonic acid was relatively unstable.

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