Naphthalenesulfonic Acids[1]

VI—Sulfonation of Naphthalene in the Vapor Phase

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A new method is described for sulfonating naphthalene. Naphthalene vapors are passed up through a cast-iron tower containing quartz stones, through which hot sulfuric acid is descending. Much less sulfuric acid is required and isomeric changes are largely prevented as the reaction product is rapidly removed from the reaction chamber. Another advantage is that the process is continuous. Experiments were conducted at temperatures varying between 220° and 245° C. Sulfuric acid of 80 to 95 per cent strength was employed. The reaction product consists essentially of naphthalene-2,7-disulfonic acid, with some naphthalene-2,6-disulfonic acid and traces of naphthalenemonosulfonic acid. Analyses show that 78 to 85 per cent of the disulfonic acids produced by this method is naphthalene-2,7-disulfonic acid. An apparatus in which the experiments were conducted is shown and described. The results obtained in a number of experiments are given.

This laboratory is now working on a method of producing H acid from 2,7-disulfonic acid in one step. If this method is found to be practical it will make use of all the 2,7-disulfonic acid produced.

THE sulfonation of naphthalene is usually effected by adding naphthalene to sulfuric acid or sulfuric acid containing sulfur trioxide under suitable temperature control and with various methods of agitation and mixing; or by adding sulfuric acid with or without sulfur trioxide to heated molten naphthalene with the proper temperature control and stirring devices. These processes are all essentially "batch operations"—that is, they are not continuous, since, when sulfonation is completed, it is necessary to remove the reaction product and clean the vessel before another batch can be made. Furthermore, in all these processes a large excess of sulfuric acid is necessary. The initial sulfonic acids formed, therefore, remain in contact with the large excess of acid at a high temperature. Under these conditions higher sulfonated bodies may be formed or isomeric compounds produced. Thus, when naphthalene is disulfonated at 160° C. the 2,7-disulfonic acid, which is first formed, under the influence of a large excess of acid and heat is converted into the worthless 2,6-disulfonic acid. If the duration of heating is short the 2,7 acid predominates, whereas if the mixture is heated for a long time this acid undergoes complete transformation into the isomeric 2,6-disulfonic acid.

Ambler and Gibbs[2] have claimed that when naphthalene is sulfonated in the vapor phase and the reaction product rapidly removed from the sulfonating reaction chamber, much less sulfuric acid is required for sulfonation and the transformation into isomeric sulfonic acids is largely prevented. This paper is a preliminary report on further studies on this problem which are being carried out in the Color Laboratory. The initial experiments were conducted in a quartz chamber, but for commercial work this is obviously not feasible. Accordingly a reaction chamber was constructed of cast iron. Preliminary experiments indicated that the cast-iron chamber would be only slightly attacked by sulfuric acid at the temperatures at which experiments were to be conducted. This has been borne out by analyses of the reaction product, which showed only about 0.4 per cent iron calculated as ferrous sulfate.

Apparatus

The apparatus (Fig. 1) consists essentially of a tower or reaction chamber, *A*, which is a cast-iron pipe 4 inches in diameter and 6 feet long. At the bottom of this tower a cap, *B*, is attached which is provided with two tubes, one serving for the introduction of naphthalene vapors and the other for the continuous discharge of the liquid sulfonation mass into the receiver *W*. Escape of the naphthalene vapors through the latter tube is prevented by means of a seal, *C*. To prevent the sulfonation mass from dropping into the naphthalene introduction tube, *D*, a deflecting hood is provided. The top of the tower is equipped with a cap, which also has two tubes. The cap is so constructed that it rests in the flange of the pipe or tower and the joint is sealed by means of asbestos packing. One tube, *E*, serves for the introduction of the acid, the other, *F*, is used to lead off the excess naphthalene vapors and the volatile products of reaction into the condensing and absorption apparatus. The tube *G* is steam-jacketed to prevent solidification of the excess naphthalene. *H* are condensers and are worthy of description here since it was found extremely difficult to condense the unchanged naphthalene vapors completely before they reached the absorption train. Unless the naphthalene vapors are thoroughly removed from the gases before they enter the absorption train the tubes are soon clogged, with subsequent clogging of the apparatus.

A lead coil is wound just to fit inside of a bell jar and several screens of large mesh are placed across the coil. Cold water is circulated continuously through the lead coil. The bell jar is fastened by means of clamps and a rubber gasket to a supporting base, which is provided with an outlet tube to drain the liquid condensate into *J*. The uncondensed gases are absorbed in the sodium hydroxide washing train, *K*. *L* is a constant-pressure bottle.

M is a steam-jacketed preheater having two separate compartments, in which the naphthalene is melted and from which it is allowed to flow under suitable control into the vaporizer, *N*, the temperature of which is maintained above the boiling point of naphthalene. *P* is a constant-flow bulb. *R* and *S* are removable plugs which permit the washing of the tower and condenser, respectively. *T* is a manometer to record the pressure in the apparatus. At *U*, gate valves are placed, as they give better results than a three-way valve.

The tower *A*, the acid lead-in *E*, and the vaporizer *N* are heated by means of suitable electric coils and the whole is covered with asbestos or magnesia pipe covering. The electric coils on the tower are in four sections which permit much flexibility and very exact temperature control. Temperatures are recorded by thermometers, *Q*, placed as shown. The whole apparatus is supported in a vertical position. Into the tower are placed round quartz stones about the size of an egg. These rest on a cast-iron tripod the top of which is drilled with numerous holes. The height of the stones

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923. Received September 21, 1923. Contribution 85, Color Laboratory.

[2] U. S. Patent 1,390,241 (September 6, 1921).

may be varied in the tower, but the length of the acid lead-in should be such that it is always within an inch from the top of the stones.

Operation

In order that the experiments may be comparable, conditions in the tower must be the same at the beginning of the experiment as at the end. To accomplish this, the tower is first "primed." This is done by starting the acid, which is preheated as it flows through *E*. The flow of the acid is kept constant by *P* and the rate of flow can be regulated by varying the length as well as the diameter of the tube *V*. Just as soon as the acid appears at *C* molten naphthalene is allowed to flow into the vaporizer *N*. The flow of naphthalene is controlled by valves, which are preferably of the needle-point type. As the acid strikes the quartz stones it is spread out over them and thus is rapidly raised to the temperature of the tower and presents a large surface for the absorption of the naphthalene vapors which rise steadily in a countercurrent through the apparatus. Any unchanged naphthalene, together with a portion of the water in the sulfuric acid and the water produced by the reaction and any other volatile reaction products, is led off through *F* into the condenser *H*. The naphthalene that is separated in *H* can be purified, dried, and used again. The absorbed naphthalene vapors are converted into sulfonic acids and together with the excess sulfuric acid descend through the tower and are discharged through the seal *C*. The flow of the naphthalene is so regulated that the vapors always fill the tower and an excess is distilling into the condenser. This insures the fact that the apparatus is operating at its maximum efficiency.

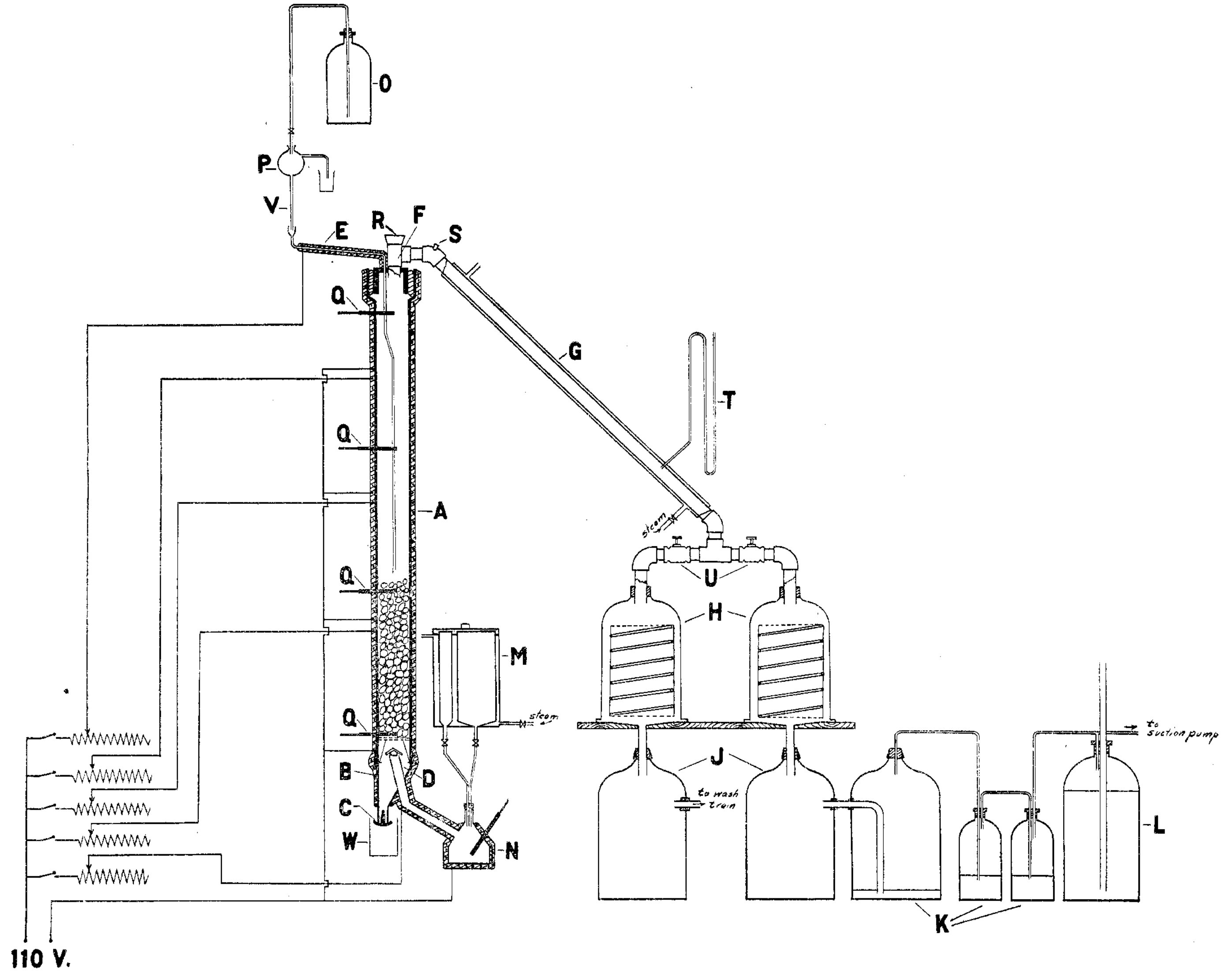

Fig. 1

This priming of the apparatus usually requires 20 to 30 minutes, after which it is ready for a quantitative experiment. The apparatus is provided with two condensers and wash trains, and two naphthalene feed compartments. One set is used for priming, the other for quantitative experiments. In order to obtain quantitative data, a weighed bottle of acid is substituted at *O*, the receiver *W* changed, the supply of priming naphthalene is cut off, and a weighed quantity of naphthalene is supplied to the vaporizer from the other compartment. At *U* the valves are reversed, the excess naphthalene is condensed in the other condenser, from which it is later removed and weighed, and the gases absorbed in weighed quantities of sodium hydroxide (in the second train). In order to overcome the back pressure at *K*, a slight suction is maintained. The manometer *T* indicates a pressure about half an inch of water less than atmospheric.

The temperatures at which these experiments can be conducted must be between the boiling point of naphthalene and the boiling point of the sulfonic acid used in each experiment. In these experiments 85 to 95 per cent sulfuric acid were employed, and therefore the temperatures chosen varied between 220° and 245° C. As first constructed the tower was filled with stones. Preliminary experiments indicated that the sulfuric acid was completely exhausted before it reached the bottom of the tower, with the result that the sulfonation mass had become so viscous that it clogged the tower. Accordingly, some of the stones were removed from the tower. A height of 2 feet was found convenient to carry on the experiments. The acid lead-in was lengthened to within an inch of the top of the stones so that experiments would be comparable. With the apparatus so constructed, it was possible to sulfonate about 500 grams of naphthalene in 1.5 to 2 hours. Thus the rate of sulfonation varied from 4 to 5 grams of naphthalene per minute. The amount of acid varied from 2.5 to 3.5 parts for every part of naphthalene used. It will be readily seen that considerable acid is saved by this method, since in the ordinary method of batch sulfonation five parts of acid are required for each part of naphthalene to produce disulfonic acids. Table I represents the conditions existing in the tower during several typical experiments.

TABLE I—CONDITIONS IN TOWER DURING SULFONATION OF NAPHTHALENE

Experiment	Temperature, ° C.	$C_{10}H_8$ used, Grams	Acid used, Grams	Duration of run, Minutes	Rate of flow of acid Grams/minute	Rate of distillation, Grams/minute	Ratio H_2SO_4 to $C_{10}H_8$	Strength of acid, Per cent	$C_{10}H_8$ recovered, Grams
49	247 ± 7	479	1785	115	15.5	4.16	3.72 to 1	90	21
50	241 ± 5	646	2270	150	15.1	4.30	3.36 to 1	90	104
51	243 ± 3	464	1580	115	13.73	4.02	3.40 to 1	90	36
52	232 ± 2	463	1600	150	10.66	3.08	3.45 to 1	90	37
54	235 ± 3	472	1450	155	9.35	3.04	3.07 to 1	90	28
55	233 ± 2	225	570	60	9.5	3.75	2.53 to 1	90	25
56	233 ± 3	463	1255	120	10.45	3.85	2.71 to 1	90	37
58	225 ± 5	458	1170	117	10.	3.91	2.55 to 1	95	42
59	233 ± 8	475	1715	120	14.3	3.95	3.61 to 1	95	25
60	225 ± 3	474	1540	115	13.4	4.11	3.25 to 1	95	26
61	224 ± 4	459	1305	83	15.72	5.53	3.84 to 1	95	41
62	222 ± 5	435	1650	90	18.3	4.83	3.79 to 1	85	65

ANALYSES OF THE REACTION PRODUCT

Besides the main reaction

$$C_{10}H_8 + 2H_2SO_4 = C_{10}H_6(SO_3H)_2 + 2H_2O$$

there is some charring. This always caused the sulfuric acid solution of the disulfonic acids to look black, but the actual amount of tar formed was never very great. Repeated efforts to isolate sulfons in many samples of the acid product were unsuccessful. There is also a reaction between hot sulfuric acid and the cast-iron tower; this takes place only to a slight extent, however. Analysis of the reaction product showed but 0.4 per cent iron calculated as ferrous sulfate. The reaction product was analyzed using Ambler's[3] method of qualitative analysis, and showed the product to consist essentially of naphthalene-2,7-disulfonic acid, a very small amount of naphthalene-2,6-disulfonic acid, and traces of naphthalene-β-monosulfonic acid.

QUANTITATIVE ANALYSIS

Since qualitative analysis indicated that the reaction product consisted essentially of disulfonic acids and sulfuric acid, a determination of the amounts of these acids was made. An aliquot of the acid run was titrated with 0.1 N sodium hydroxide. To another aliquot was added the calculated amount of barium hydroxide necessary to neutralize the solution exactly. This second mixture was evaporated to dryness and the barium salts were dehydrated at 200° C. and weighed. With the two results obtained and with the aid of the following formula, the proportion of sulfuric acid to disulfonic acid can be readily calculated.

If m = grams of mixed anhydrous barium salts obtainable from acid run
b = grams of $Ba(OH)_2$ necessary to neutralize acid run
x = grams of $BaSO_4$ in m
y = grams of $Ba(SO_3)_2C_{10}H_6$ in m,

then the amount of barium disulfonate in the mixed salts may be found by using the following equations:

$$x + y = m$$

$$\frac{Ba(OH)_2}{BaSO_4} \cdot x + \frac{Ba(OH)_2}{Ba(SO_3)_2C_{10}H_6} \cdot y = b$$

Solving these equations simultaneously for y and converting to disulfonic acid, the weight of disulfonic acids is $1.52m - 2.07b$.

When attempts were made to titrate an aliquot of the acid run with sodium hydroxide employing the common indicators, it was found that the dark color of the solution interfered to such an extent that accurate results were impossible. Numerous attempts to remove this color failed. Resort was finally had to an electrometric titration apparatus, which gave satisfactory results.

The quantitative determination of the respective amounts of the two isomeric disulfonic acids present in the acid runs was then attempted. The only applicable method at hand was that which depended upon the varying solubility of lead-2,7-disulfonate in the presence of lead-2,6-disulfonate.[4]

At this point the tar in the acid runs, although present in small quantities, introduced another difficulty. The solubility of pure anhydrous lead-2,7-disulfonate is 8.2 parts in 100 parts of water at 25° C., but the solvent effect of the small quantity of tar increased the determined solubility of lead disulfonate to over 10 parts per 100 parts of water, thus vitiating any results obtained by this method. The removal of the tar present was therefore necessary for the application of this quantitative method of analysis. The tar removal was accomplished by hydrolysis with steam and absorption with decolorizing charcoal.[5] After the removal of the tar by this method the quantitative method of analysis outlined above was found applicable.

Table II gives the results obtained employing this method.

TABLE II—RESULTS OF SULFONATION OF NAPHTHALENE IN THE VAPOR PHASE

Experiment	Acid run, Grams	$Ba(OH)_2$ to neutralize, Grams	Dried barium salts, Grams	H_2SO_4 present, Per cent	Disulfonic acid present, Per cent	Yield of disulfonic acid from $C_{10}H_8$ consumed, Per cent	2,7-disulfonic acid in disulfonic acids produced, Per cent
49	1715	2391	3185.7	55.33	44.27	70.4	83.9
50	2225	2684.5	3559.1	56.90	42.50	65.1	82.4
51	1530	1412	2486.7	44.36	55.24	80.9	79.9
52	1540	1610.7	2747.1	45.76	53.34	79.6	82.2
54	1350	1247.7	2277.6	35.30	64.30	81.7	78.9
55	600	573.4	1036.0	35.74	63.86	75.6	75.0
56	1200	1065.7	2032.4	26.83	72.77	83.8	80.6
58	1295	1237.5	2215.5	38.18	61.42	77.2	85.9
59	1810	1636.6	2651.5	62.30	37.30	59.0	72.6
60	1715	1916.7	3144.0	53.09	46.51	74.8	78.2
61	1600	1677.9	2821.5	49.43	50.17	77.7	80.7
62	1685	1857.7	3013.0	56.80	42.80	73.7	79.9

The table shows that the yields vary from 59 to 83 per cent of the theory, based on the naphthalene consumed in the apparatus. There appears to be no relation between the ratio of sulfuric acid to naphthalene and the yield of disulfonic acid based on the naphthalene consumed. The temperature range of 25° C. also seems to have no effect on the yield of disulfonic acid. Moreover, no relation is apparent between the ratio of acid to naphthalene, temperature, and the tar formed.

It has been found that when less than 2.5 parts of sulfuric acid to 1 part of naphthalene are employed, the sulfonation mass becomes so viscous that the tower is soon clogged. With 3 to 3.5 parts of acid to 1 part of naphthalene and with the conditions as outlined above, yields of 77 to 80 per cent disulfonic acid can be obtained. Of the disulfonic acids produced under these conditions the percentage of 2,7-disulfonic acid varied from 78 to 85.

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[3] THIS JOURNAL, **12**, 1085 (1920).

[4] THIS JOURNAL, **16**, 273 (1924).

[5] Ambler and Lynch, "Elimination of Soluble Tar from Sulfonation Masses," to appear in a subsequent issue.