

From our experiments we assume  $d[C_{\text{HBr}}]/dt = kC_{\text{HBr}} \cdot C_A$ . It is also necessary to assume  $G = KC_{\text{HBr}}$ . From these,  $d[C_{\text{HBr}}]/dt = dG/Kdt = (kG/K)C_A$  or  $dG/dt = kGC_A$ . Integrating this equation and determining the value of the constant of integration by assuming a conductance due to a concentration of hydrogen bromide at the start of the reaction, we get  $\ln G = kC_A t + \ln G_0$ , or passing to decimal logarithms and placing  $C_A = 1.874$  moles per liter

$$\log G = \frac{1.874}{2.303} kt + \log G_0 = 0.8138 kt + \log G_0$$

We can determine the numerical value of the velocity constant by plotting  $\log G$  versus  $t$ , measuring the slope of the straight line obtained and dividing this value by 0.8138.

The author wishes to acknowledge his indebtedness to Dr. H. S. Van Klooster, Professor of Physical Chemistry at the Rensselaer Polytechnic Institute, under whose direction the investigation was carried out.

### Summary

The kinetics of the bromination of acetone in organic solvents has been investigated.

Water has a powerful retarding influence on this reaction.

The extraordinary catalytic power of dry hydrogen bromide on the bromination of acetone is demonstrated.

The reaction is approximately first order with respect to hydrogen bromide.

A considerable change in the dielectric constant of the solutions used has been observed during the progress of this reaction.

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[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

## SULFONATION OF 2-NAPHTHOL IN PRESENCE OF BORIC ACID. 2-NAPHTHOL-1,6-DISULFONIC ACID

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The use of boric acid as a catalyst in the sulfonation of 2-naphthol (one part of boric acid for two hundred parts of naphthol), for the purpose of improving yields and quality of the reaction products, has been patented by M. L. Crossley and G. S. Simpson.<sup>1</sup>

Two years before issue of the patent, the writer experimented in a similar direction, and observed that appreciable amounts of boric acid caused a striking change in the expected reaction course. A difference became outwardly noticeable—sulfonation masses, instead of remaining fluid, solidi-

<sup>1</sup> Crossley and Simpson, U. S. Patent 1,570,046 (1926).

fied rapidly. With limited amounts of sulfuric acid the reaction led to the formation of 2-naphthol-1-sulfonic acid as a permanent, instead of a transitory, stage which in practice is rather difficult to arrest. Greater amounts of acid yielded mainly 2-naphthol-1,6-disulfonic acid, besides smaller amounts of the 8-sulfonic (Croceine) acid and only a few per cent. of the 6-sulfonic (Schaeffer) acid.

Fixed yield ratios of these three products, for definite reaction temperatures, were observed when one molecular weight of boric acid was used for three of naphthol. With gradually decreased amounts of boric acid, yield ratios changed continually; greater amounts had no further effect. Conceivably, then, formation of a trinaphthyl-boric ester preceded sulfonation. It may have been the sulfonated ester which caused solidification of sulfonation masses, but it decomposed immediately with water or ice.

The formation of 2-naphthol-1,6-disulfonic acid, though unlooked for, was in accord with the normal substitution tendencies of 2-naphthol, which may yield, as is well known, the 1-, the 6- and the 8-monosulfonic, the 3,6- and the 6,8-disulfonic and the 3,6,8-trisulfonic acids, no other but the 1-, 3-, 6- and 8-hydrogen atoms being replaceable upon direct sulfonation of the naphthol.

The 1,6-disulfonic acid, undoubtedly, has been known for many years, but has received no more than cursory mention.<sup>2</sup> Presumably the product here referred to was prepared from the well-known naphthylamine-1,6-disulfonic acid.<sup>3</sup> More recently, J. Pollak and E. Blumenstock-Halward<sup>4</sup> prepared the 2-naphthol-1,6-disulfonyl chloride through the action of chlorosulfonic acid on naphthol or naphthol-6-sulfonic acid. Saponification of the chloride in alcoholic solution gave a tribarium and a tripotassium salt of the 1,6-disulfonic acid.

The 1,6-disulfonic acid resembled, in its chemical behavior, the naphthol-1-sulfonic acid. It could not be isolated as a free acid, but either sodium or potassium chloride precipitated it from solution in the form of its metal salts.

The sulfonic acid group in the 1-position prevented a smooth coupling with diazonium compounds, though more reactive ones, like *p*-diazobenzene, were capable of displacing the obstructing sulfonic acid group. The hydrolytic action of dilute acids likewise eliminated the same sulfonic acid group readily, at about 85°.

The ease with which the 1,6-disulfonic acid formed and its stability during sulfonation in presence of boric acid suggested that this product might also occur in sulfonations without the use of boric acid. It was indeed found to be a by-product in straight sulfonations at temperatures up to 75°,

<sup>2</sup> H. Th. Bucherer, *J. prakt. Chem.*, [2] 177, 69-73 (1904); German Patent 117,471, and British Patent 1387 (1900).

<sup>3</sup> Forsling, *Ber.*, 21, 3495 (1888).

<sup>4</sup> J. Pollak and E. Blumenstock-Halward, *Monatsh.*, 49, 203 (1928).

and could be obtained as the main reaction product at temperatures under 18°. This observation made it possible, for the first time, to account for practically all of the conversion products of naphthol in sulfonation methods, which have long been used in the commercial production of the 8- and 6-sulfonic and of the 6,8- and 3,6-disulfonic acids. (Higher sulfonation temperatures lead to other, poorly explained losses through destructive oxidation and perhaps through the formation of dehydration products of naphthol.)

A number of sulfonations were made, with or without addition of boric acid, to determine the specific influence of the latter, and to find the most suitable conditions for the preparation of the commercially important 2-naphthol-1-sulfonic and of the 1,6-disulfonic acid. The product yields of a few representative experiments have been tabulated below.

TABLE I  
SULFONATION IN PRESENCE OF BORIC ACID

No. I	Naphthol/acid ratio, by wt.	Temp., °C.	Time	Product yields, percentage of sulfonated naphthol			
				1-	6-	8-	1,6-di-
a <sup>a</sup>	1 to 2, 100% H <sub>2</sub> SO <sub>4</sub>	20-28	4 Min.	90	9	Trace	..
b	1 to 2, 94.2% H <sub>2</sub> SO <sub>4</sub>	30	24 Hr.	74	3	10	13
c	1 to 1.73, 94.2%	30	24 Hr.	83	3	5	9
d	1 to 10, 94.2%	0	30 Hr.	Trace	2	17	81
e	1 to 5, 94.2%	25	30 Hr.	Trace	3	21	76
f	1 to 3, 94.2%	45	30 Hr.	..	4	24	72
g	1 to 2, 94.2%	85	1 Hr.	..	20	27	53

<sup>a</sup> Incomplete reaction.

TABLE II  
STRAIGHT SULFONATION

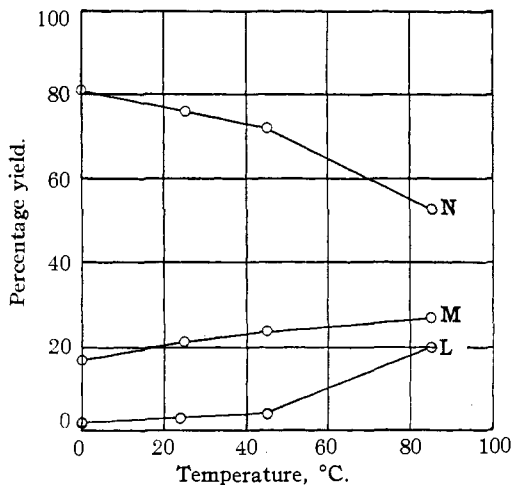
No. II	Naphthol/acid ratio, by wt.	Temp., °C.	Time	Product yields, percentage of sulfonated naphthol			
				1-	6-	8-	1,6-di-
a <sup>a</sup>	1 to 2, 100% H <sub>2</sub> SO <sub>4</sub>	20-30	4 Min.	62	12	17	9
b	1 to 10, 94.2% H <sub>2</sub> SO <sub>4</sub>	2	24 Hr.	..	3	23	74
c	1 to 8, 94.2%	13	24 Hr.	..	7	31	61
d	1 to 5, 94.2%	18	24 Hr.	..	11	38	51
e	1 to 2, 94.2%	25	24 Hr.	..	23	54	23
f	1 to 2, 94.2%	28	24 Hr.	..	28	55	17
g	1 to 2, 94.2%	32	24 Hr.	..	33	54	12
h	1 to 2, 94.2%	45	24 Hr.	..	38	49	11
i	1 to 1.5, 94.2%	56	24 Hr.	..	47	46	7
k <sup>b</sup>	1 to 1.3, 94.2%	75	24 Hr.	..	60	28	1
l <sup>b</sup>	1 to 1.1, 94.2%	85	24 Hr.	..	74	11	..

<sup>a</sup> Incomplete reaction. <sup>b</sup> Unaccounted loss.

### Discussion of Results

**2-Naphthol-1-sulfonic Acid.**—Sulfonation of brief duration, in presence of boric acid (Ia), led to the formation of only two products, the 1- and the 6-sulfonic acids, the former in a very attractive yield ratio. An appreciable quantity of naphthol, however, remained unsulfonated (though

completely dissolved). If the time was extended, disulfonation took place as long as a sufficient concentration of sulfuric acid was available. For a most advantageous procedure the sulfuric acid concentration had to be so chosen as to allow complete sulfonation and, at the same time a minimum of disulfonation (Ic). To avoid all disulfonation did not appear feasible or even desirable, since the disulfonic acid could be more easily removed from the main product than the alternative by-product, the 6-sulfonic acid of



N, 1,6-Disulfonic acid; M, 8-sulfonic acid;  
L, 6-sulfonic acid.

Fig. 1.—Sulfonation in presence of boric acid.

two, in part at least, were rearrangement products of the former. The three products formed equilibrium mixtures, in which their yield ratios depended on the reaction temperatures. This relationship may be most conveniently illustrated by a graphic representation of data given in the preceding tables (Figs. 1 and 2). A further transformation of the three products into the 3,6- and 6,8-disulfonic acids proceeded very slowly below 35°, but more and more rapidly with rising temperatures. Where this change was not desired, the effect of higher temperatures could be counteracted, as is done in practice, by decreasing the reaction time or the acid concentration, or both.

Sulfonations in the presence of boric acid showed a very gradual change in yield ratios over the entire practical temperature range; the 1,6-disulfonic acid always predominated.

Striking peculiarities in the relationships between the three reaction products were observed in straight sulfonations (Fig. 2). Between 0 and 18° yields of the disulfonic acid were surprising large. They decreased abruptly, however, within a narrow temperature range, the graph suggest-

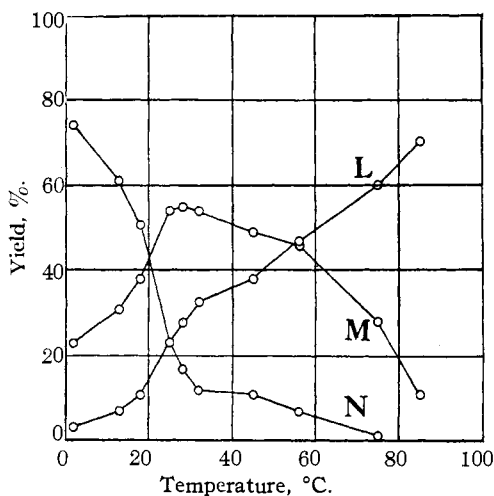
Experiment Ia. Seventy-four per cent. of the naphthol could be recovered in the form of a 1-sulfonic acid, which was free from all but traces of isomers, by precipitating it from solution with sodium chloride and by washing the isolated sodium sulfonate with a saturated solution of the chloride.

**2-Naphthol-1,6-disulfonic Acid.**—Sulfonations with concentrations of sulfuric acid sufficiently large to change all of the 1-sulfonic acid led to mixtures of the 1,6-disulfonic, the 6- and the 8-sulfonic acids. The latter

ing the existence of a critical temperature, at about 22°, above which the disulfonic acid molecule was no longer stable, but changed, rather impartially, into either the 6- or the 8-sulfonic acid. A conversion into the former, through hydrolysis of the 1-sulfonic group, might well be expected; a rearrangement into the 8-sulfonic acid should require a rather complicated mechanism.

The 2-naphthol-1,6-disulfonic acid could be prepared in practical yields either by a straight sulfonation or with the addition of boric acid, the latter method being the more convenient for its greater economy in materials and for the ease with which it may be controlled. Sulfonation at 45°, (If), appeared to be most suitable. The quantity of sulfuric acid used in this experiment might be further reduced by substituting a more concentrated (100%) acid.

Straight sulfonation experiments indicated that a reaction temperature of 25 to 30°, instead of the customary 45°, was most favorable for the commercial production of 2-naphthol-8-sulfonic acid, a maximum yield of the more expensive of the two isomers being obtained within this range. The by-product 1,6-



L, 6-Sulfonic acid; M, 8-sulfonic acid; N, 1, 6-disulfonic acid.

Fig. 2.—Straight sulfonation.

disulfonic acid could be conveniently hydrolyzed into 6-sulfonic acid by heating the diluted sulfonation mixture to 85°.

The 3,6- and 6,8-disulfonic ("R" and "G") acids require sulfonation temperatures at which the 1,6-isomer occurs in negligible amounts or not at all. Of interest might be a comparison of sulfonations, with or without addition of boric acid, at 135°. Sulfonation with three parts of concd. sulfuric acid to one of naphthol, at twenty-four hours' duration and in the presence of boric acid, yielded 28% of the 1,6-, 31% of the 6,8- and 39% of the 3,6-disulfonic acids. A straight sulfonation, under parallel conditions, gave 33% of the 6,8- and 43% of the 3,6- isomers, but no trace of the third isomer. The loss through destructive oxidation and other causes was considerable in this case, but negligible in the sulfonation with boric acid.

### Experimental Part

**Materials.**—Resublimed 2-naphthol, which contained less than 0.1% of the isomeric naphthol, and pure concentrated sulfuric acid (94.2%) were used in sulfonations.

Acid of 100% strength was prepared by mixing calculated amounts of fuming and of concentrated acids. Pure boric acid was dehydrated at 110°; the resulting metaboric acid was readily soluble in sulfuric acid at 100 to 120° and was preferred to avoid unnecessary dilution of the sulfonating agent. The glassy boron trioxide dissolved with difficulty, and for that reason was not used.

**Analytical methods** for determining the various naphthol-sulfonic acids in mixtures were based on well-known industrial methods of selective coupling with diazonium compounds.<sup>5</sup> Thus the 6- and 8-isomers were determined by titrating the former with a molal solution of *p*-diazotoluene and continuing titration of the 8-sulfonic acid by coupling it with a *p*-nitro-diazobenzene solution. Simple mixtures of these two isomers could thus be analyzed with considerable accuracy. For sulfonation mixtures, however, which contained the 1-sulfonic or the 1,6-disulfonic acid in addition, a few precautions had to be observed. These acids tended to combine with the more active diazonium compounds into peculiar addition products, highly soluble, but more unstable and of much lower color intensity than true azo dyes. Their formation could be practically eliminated by carrying out the titrations at low temperatures, between 0 and -5°, and especially by avoiding a high degree of alkalinity in the solution. No references for determining either the 1-sulfonic, or the 1,6-disulfonic acid in mixtures with other naphthol sulfonic acids appeared to be available, and a simple method therefore had to be devised. Fortunately, the sulfonic acid group in the 1-position may easily be eliminated by hydrolysis with acids at temperatures near the boiling point of water, and the resulting naphthol or naphthol-6-sulfonic acid may then be determined by the usual coupling methods. Sulfonic acid groups in the 6-, as well as in the 8-position, completely resisted hydrolytic action of acids under the time and temperature conditions employed. Artificial mixtures of pure 6- and 1-sulfonic acids, and of 6-sulfonic and 1,6-disulfonic acid, could be determined with an accuracy of better than 1% by such a method.

Standard diazonium solutions were prepared by dissolving 0.1 mole of pure *p*-toluidine, or of *p*-nitro-aniline, respectively, in an excess of hydrochloric acid, and subsequent diazotization with the customary precautions. The solutions were diluted to one liter and standardized by titrating weighed amounts of pure naphthol dissolved in sodium hydroxide solution to which an excess of carbonate was added. Only freshly prepared diazonium solutions were used in titrations.

**Procedure.**—Sulfonations were carried out in flasks of 125-cc. capacity with a thermometer through an airtight stopper. Weighed amounts of sulfuric acid, or of sulfuric-boric acid mixture, were cooled below the intended equilibrium temperature, generally to about 10°. Accurately weighed naphthol was placed in the flask in one addition and stirred into solution by means of the thermometer. Sulfonations at such lower temperatures proceeded slowly and could easily be controlled by occasional outside cooling. The temperature was allowed to rise gradually to the desired level, but never over. With boric acid present, sulfonation masses soon became extremely viscous and hardened after about thirty minutes' agitation, which was just sufficient to dissolve the finely divided naphthol. The flasks were tightly stoppered to prevent entrance of moisture and were partly immersed in a water-bath, which was maintained at a definite temperature, within one degree. Sulfonations over 35° were kept in an air-bath with automatic control, which maintained the desired temperature within two degrees. All experiments were made in duplicate. Procedure and analytical methods were varied as little as possible; representative experiments only need therefore be described.

<sup>5</sup> Compare Fierz, "Farbenchemie," Zürich, 1920, pp. 296 ff.

### 2-Naphthol-1-sulfonic Acid

**Experiment Ia.**—A solution of 1.50 g. of metaboric acid in 30.0 g. of 100% sulfuric acid was cooled to 15°, and 14.40 g. of naphthol (0.1 mole) dissolved in it by vigorous stirring. Through outside cooling, the temperature was kept at 20 to 28° for the larger part of four minutes, the total duration of the reaction. At the end of this time, the naphthol had practically dissolved; the sulfonation mass was still fluid. Rapid dilution with ice and water arrested the reaction. The total volume of the diluted mass was brought up to 250 cc. exactly.

Un sulfonated naphthol, in suspension, was removed by filtration and the clear filtrate saved for subsequent determinations of sulfonated products. The recovered naphthol, properly washed, was dissolved in an equivalent amount of sodium hydroxide solution (thiazole indicator), and an excess of sodium carbonate added. Definite portions of the solution, one-fourth in this case, were titrated with 0.1 *M* *p*-diazotoluene hydrochloride solution, which required 68.6 and 68.7 cc., corresponding to a total of 0.0274 mole of unchanged naphthol. The remainder, 0.0726 mole, had therefore been sulfonated.

Naphthol-1-sulfonic acid was precipitated from the solution of sulfonated products by addition of sodium chloride, isolated and recrystallized. Its identity was established by its ferric chloride reaction (reddish blue coloration), the absence of fluorescence in alkaline solution, and by the ease with which it changed into naphthol and sulfuric acid on warming with dilute mineral acids. It coupled slowly, in the presence of alkali, with *p*-nitro-diazobenzene, yielding an oil-soluble, un sulfonated orange dye.

The solution of sulfonated products contained naphthol-6-sulfonic and traces of 8-sulfonic acids in amounts too small for isolation. These isomers were recognized by their behavior with diazonium compounds, the 6-sulfonic acid also by comparing the azo dye resulting through coupling with *p*-diazotoluene with a dye of known origin.

### Analytical Determinations

**Naphthol-6-sulfonic Acid.**—One-fifth portions of the sulfonated products, 50 cc., were neutralized and an excess of sodium bicarbonate was added. The 6-sulfonic acid present required 12.6 and 12.8 cc. of 0.1 *M* *p*-diazotoluene hydrochloride solution, which corresponded to 63.5 cc. for the total solution. Of the sulfonated naphthol, 0.0064 mole or 8.8% had reacted to form 6-sulfonic acid.

**Naphthol-1-sulfonic Acid.**—A 50-cc. portion of sulfonation products was mixed with an equal volume of water and with 10 cc. of concd. hydrochloric acid, the solution gently refluxed for twenty minutes, then cooled and further diluted. Naphthol, produced through hydrolysis of the 1-sulfonic acid, was isolated by filtration, washed and determined by titration in an alkaline solution as described before. Two portions required 131.4 and 129.7 cc., respectively, of 0.1 *M* *p*-diazotoluene solution, equivalent to a total of 651 cc., or to 0.0651 mole of 1-sulfonic acid, or to 90% of the sulfonated naphthol.

**Naphthol-8-sulfonic Acid.**—The filtrate from the hydrolyzed naphthol was neutralized with an excess of sodium bicarbonate, the 6-sulfonic acid present titrated with 0.1 *M* *p*-diazotoluene solution, 12.4 and 12.5 cc. being consumed. This result was in good agreement with the previous determination in which original samples not subjected to hydrolysis had been used, which indicated that the naphthol-1,6-disulfonic acid could not have been formed to any extent during the short period of sulfonation. Naphthol-8-sulfonic acid was now determined by continuing the titration with 0.1 *M* *p*-nitrodiazobenzene solution, no more than 0.3 cc. being sufficient to reach an end-point—only a trace of the 8-sulfonic acid could have been present.

To summarize results, sulfonation under the conditions of the experiment had

yielded mainly naphthol-1-sulfonic acid, 90% of the sulfonated naphthol being thus accounted for. Small amounts of the 6-sulfonic (8.8%) and traces of the 8-sulfonic acids were formed besides. Parallel sulfonations gave closely similar results even though the amounts of naphthol actually sulfonated varied between 0.073 and 0.082 mole.

### Practically Obtainable Yield of Naphthol-1-sulfonic Acid

**Experiment Ic.**—A solution of 3.00 g. of metaboric acid in 50.0 g. of 94.2% sulfuric acid was cooled to 15°. Two-tenths mole of naphthol, 28.80 g., was stirred into the acid, the temperature of the mass being allowed to rise gradually to 25°. The naphthol solution, at first reddish brown, changed color, became extremely viscous, and hardened to a yellowish solid at the end of thirty minutes. The mass was kept at 28° for twenty-four hours. It was then dissolved, in small chips, in ice and water and the volume of the solution filled up to 250 cc. The naphthol had been sulfonated with the exception of a negligibly few larger particles. The yields of the reaction products were analytically determined—83% of the theoretically possible amount of 1-sulfonic, 3% of 6-sulfonic, 5% of 8-sulfonic and 9% of 1,6-disulfonic acids being found.

**Isolation of Naphthol-1-sulfonic Acid.**—One-half of the solution, which contained one-tenth mole of sulfonated naphthol, and 25 g. of sodium chloride were stirred together for twelve hours. The precipitated sodium salt of the 1-sulfonic acid was gathered on a suction funnel and repeatedly washed with small portions of saturated chloride solution, 125 cc. in all being used. The washed product contained a trace of mineral acid and gave a very faint reaction for 6-sulfonic acid with *p*-diazotoluene. For analytical determination, exactly one-tenth of the material, dissolved in 50 cc. of water and 15 cc. of concd. hydrochloric acid, was refluxed for twenty minutes, the liberated naphthol isolated and determined as usual. Two such portions, from exactly parallel sulfonation experiments, required 72.2 and 73.6 cc. of 0.1 *M* *p*-diazotoluene solution. The yield of *isolated*, useful product therefore corresponded to about 73% of the naphthol used.

### 2-Naphthol-1,6-disulfonic Acid

**Experiment If.**—Two-tenths mole of naphthol, or 28.80 g., was stirred into a solution of 3.00 g. of metaboric acid in 87.0 g. of 94.2% sulfuric acid. The temperature of the mixture was allowed to rise from 15°, at the beginning, to 30°. At the end of twenty minutes the mass solidified. It was maintained at 45° for thirty hours. In the process of disulfonation the material changed from a yellowish to a light gray coloration and softened a little. It was diluted with ice and water to a volume of exactly 250 cc. The analysis of test portions indicated the presence of small amounts of 6-sulfonic (4%) and of 8-sulfonic acids (24%). The main product of the reaction was the 1,6-disulfonic acid. Its dipotassium salt could be prepared in excellent yield and practically free from foreign admixtures in one operation by precipitating it with potassium acetate, and by washing the isolated material first with a 20% solution of acetate and then with ethyl alcohol to remove the acetate. A further recrystallization from water yielded crystals with one molecule of water, small slender prisms with a tendency to arrange in clusters. All faces appeared to be inclined at right angles toward each other, the crystals, presumably, possessing orthorhombic symmetry.

*Anal.* Calcd. for  $C_{10}H_6O_7S_2K_2 \cdot H_2O$ : S, 16.06; K, 19.63;  $H_2O$ , 4.52. Found: S, 15.98; K, 19.52; loss on drying at 90°, 4.47.

The disodium salt was precipitated from the solution of sulfonic acids with sodium chloride. It was isolated by filtration, washed with a saturated chloride solution to remove by-products and mineral acids and after complete neutralization recrystallized from hot water until free from chloride. It crystallized with three molecules of water



and formed thin, elongated plates which had the characteristics of the triclinic system. Crystals of a centimeter's length could easily be produced.

*Anal.* Calcd. for  $C_{10}H_6O_7S_2Na_2 \cdot 3H_2O$ : S, 15.94; Na, 11.44;  $H_2O$ , 13.44. Found: S, 15.85; Na, 11.38; loss on drying at  $70^\circ$ , 13.55.

**Properties and Constitution.**—The disulfonic acid gave a clear, reddish blue coloration with ferric chloride solution. It did not form nitroso derivatives, nor was it capable of combining with diazobenzene, which appeared to indicate that one of the two sulfonic acid groups occupied the 1-position. Indeed, the more reactive nitrodiazobenzene coupled slowly, in the course of several hours, by displacing the obstructing sulfonic acid group. A monosulfonated orange dye and mineral sulfate resulted. The same sulfonic acid group could be removed through hydrolytic action of dilute mineral acids at  $85$  to  $90^\circ$ , the disulfonic acid reacting, in this respect, with the same ease as the naphthol-1-sulfonic acid, but quite unlike all the other known sulfonic acids (which hydrolyze at about  $135^\circ$ ).

The product which remained after losing the mobile sulfonic acid group was found to be identical with 2-naphthol-6-sulfonic acid. It was recognized by comparing the azo dyes which resulted from coupling with diazobenzene and *p*-diazotoluene against dyes of known constitution. Its nitroso derivative, in conjunction with ferric chloride, yielded a characteristic green dye.<sup>6</sup> For further identification, the well-characterized free acid was prepared directly from the sulfonation products. These, it will be remembered, already contained a small amount of the 6-sulfonic acid. A somewhat quantitative as well as a qualitative determination of this product was therefore necessary.

One-tenth of the sulfonation products, 25 cc. of the solution, and 75 cc. of concd. hydrochloric acid, mixed, remained perfectly clear in the cold. After heating at  $90^\circ$ , for twenty minutes, a heavy precipitate, the 6-sulfonic acid, separated. It was collected on a suction filter and thoroughly washed with concd. hydrochloric acid until practically free from sulfuric acid. The crystals were redissolved in water and the solution was divided exactly in halves. One of these portions was saturated with hydrogen chloride, the reprecipitated product isolated and dried over technical potassium hydroxide sticks. The resulting material had the same composition and melting point ( $118^\circ$ ) as the 2-naphthol-6-sulfonic acid  $\cdot 2H_2O$  prepared by Engel and Hutchison.<sup>7</sup> The monohydrate (m. p.  $129^\circ$ ) and the completely dehydrated material (m. p.  $167^\circ$ ) were also obtained upon more vigorous drying.

The second portion of the 6-sulfonic acid solution (which originated from 0.01 mole of naphthol) was neutralized and titrated, in the presence of sodium bicarbonate, with 0.1 *M* *p*-diazotoluene solution. This required 64 cc., which corresponded to a recovery of 64% of the naphthol in the form of pure 6-sulfonic acid. With the exception of one-sixteenth, at the utmost, this quantity could have originated only through hydrolysis of the 2-naphthol-1,6-disulfonic acid.

The ease with which this disulfonic acid hydrolyzed made a quantitative determination a simple task. One-twentieth of the sulfonation products, 12.5 cc. of the solution, was further diluted, neutralized and mixed with sodium bicarbonate. The 6-sulfonic acid, formed as a primary sulfonation product, consumed 4.3 and 4.2 cc. of 0.1 *M* *p*-diazotoluene solution. Another 12.5-cc. portion was mixed with 40 cc. of water and 10 cc. of concd. hydrochloric acid and the mixture gently refluxed for twenty minutes. After dilution, neutralization and addition of sodium bicarbonate, the 6-sulfonic acid now present required 76.3, 75.8 cc. of the *p*-diazotoluene solution. The difference between titrations before and after hydrolysis, 71.8 cc. in average, represented the

<sup>6</sup> Society of Dyers and Colourists, "Colour Index," 1924, No. 5.

<sup>7</sup> K. H. Engel and A. W. Hutchison, THIS JOURNAL, 52, 211 (1930).

amount of 1,6-disulfonic acid originally in solution, and indicated a conversion of approximately 72% of the naphthol into this product.

**Practically Obtainable Yield of 1,6-Disulfonic Acid.**—One-half of the sulfonation products, or 125 cc. of solution, and 25 g. of sodium chloride were stirred for twelve hours, a heavy, crystalline precipitate was isolated by filtration and washed with 125 cc. of saturated chloride solution. The disodium salt of the 1,6-disulfonic acid thus obtained was practically free from other sulfonation products. Portions of it were submitted to the hydrolytic action of dilute hydrochloric acid and the generated naphthol-6-sulfonic acid determined as before. This titration indicated a recovery of 64% of the naphthol in the form of the disodium salt of the 1,6-disulfonic acid.

**Other Sulfonation Products.**—Naphthol-6-sulfonic acid, formed in small amounts, could be isolated only in form of an azo dye obtained through coupling with *p*-diazotoluene. Dyeings upon wool or silk apparently agreed in shade and intensity with dyeings of a pure compound prepared from known intermediates and recrystallized from ethyl alcohol. An unsuccessful search was made for very small amounts of the unknown 2-naphthol-3-sulfonic acid.

Naphthol-8-sulfonic acid, although formed in appreciable amounts, likewise resisted isolation on account of the extreme solubility of its metal salts. It also was changed into an azo dye. A portion of the sulfonation products was titrated with *p*-diazotoluene solution until all 6-sulfonic acid present had combined. The resulting scarlet dye was precipitated with sodium chloride and removed by filtration. The weakly colored filtrate, which contained the 8-sulfonic acid, was mixed with its exact equivalent of diazobenzene hydrochloride solution; all combinations, of course, were carried out in the presence of sodium bicarbonate and at the freezing point. The precipitated orange dye was isolated and dried. It showed pronounced solubility in ethyl alcohol, and separated from a hot saturated solution in well-formed slender prisms which were obliquely cut and belonged, apparently, to the monoclinic system. The product agreed in all characteristics with a dye prepared from a known sample of 8-sulfonic acid.

The 2-naphthol-8-sulfonic acid was quantitatively determined by titration with 0.1 *M* *p*-nitrodiazobenzene solution.

Sulfonations under varying conditions were investigated in a similar manner as described in the preceding pages. Wherever the actual quantities of reaction product were small, their isolation was not attempted.

### Summary

The presence of boric acid during sulfonations of 2-naphthol caused no changes in the familiar substitution tendencies of the naphthol, but influenced the yield ratios of commonly concurring reaction products decidedly.

Its presence favored the retention of the loosely held 1-sulfonic acid group in the naphthol-1-sulfonic and the 1,6-disulfonic acids.

The same disulfonic acid was found to be a by-product of ordinary, straight sulfonations at temperatures up to 75°. It formed the main reaction product in sulfonations under 18°.

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