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THE SULFONATION OF PARA-CYMENE

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When *p*-cymene, 1-methyl-4-*iso*propyl-benzene, is sulfonated, two isomeric monosulfonic acids are possible (neglecting, of course, substitution in the side chains), one with the sulfonic group adjacent to methyl, sometimes referred to in the literature as the alpha acid, the other with the sulfonic group *ortho* to *iso*propyl or the beta acid. The α acid on fusion with alkali is converted into carvacrol, whereas the β acid yields thymol. In the sulfonation of *p*-cymene as it is usually carried out the α acid is the principal product obtained; in fact, the earlier workers, such as Delalande,[1] Sieveking,[2] Beilstein and Kupffer,[3] assumed that only one acid was formed. The possibility of the formation of both of these acids in the course of the sulfonation of *p*-cymene was first clearly recognized by Jacobsen.[4] He sulfonated *p*-cymene with concd. sulfuric acid at 90° to 100° and with fuming sulfuric acid at 0°. The barium sulfonates were subjected to repeated fractional crystallizations, but no isomeric barium cymenesulfonate could be detected. Claus and Cratz,[5] however, in a preliminary paper published in 1880 maintained that both acids are formed when cymene is sulfonated. In the following year, Claus[6] claimed to have actually isolated both acids from a sulfonation product of *p*-cymene. He treated cymene with 5 parts of concd. sulfuric acid and heated the mixture on the water-bath for six to eight hours. The barium salts of the sulfonic acids were subsequently subjected to fractional crystallization and from the last fraction, after removal of the barium salt of cymene disulfonic acid, the salt of the β acid was obtained. However, no crystalline sulfonamide was isolated, presumably due to impurities present. The sulfonamide of the β acid (prepared by sulfonating 2-bromocymene and subsequently removing the bromine with sodium amalgam) was later found by Remsen and Day[7] to be a crystalline compound melting at 148° (uncorr.). Schorger[8] following the method of Claus for the separation of the two acids obtained a yield of 14.6% of the β acid. Neither Claus nor Schorger seems to have made any close study of the conditions favorable for the production of either isomer. In connection with the work done in

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[1] Delalande, *Ann.*, **38**, 342 (1841).

[2] Sieveking, *Ann.*, **106**, 258 (1858).

[3] Beilstein and Kupffer, *Ann.*, **170**, 287 (1873).

[4] Jacobsen, *Ber.*, **11**, 1058 (1878).

[5] Claus and Cratz, *Ber.*, **13**, 901 (1880).

[6] Claus, *Ber.*, **14**, 2140 (1881).

[7] Remsen and Day, *Am. Chem. J.*, **5**, 154 (1883).

[8] Schorger, *J. Ind. Eng. Chem.*, **10**, 259 (1918).

this Laboratory on the synthesis of thymol from *p*-cymene, it became of interest to know the relative amount of each sulfonic acid formed under various conditions, and accordingly the experiments recorded in this paper were carried out.

Experimental Part

In order to study the sulfonation of *p*-cymene with particular reference to the relative quantity of each sulfonic acid formed under a given set of conditions it was necessary to devise an analytical method suitable for the estimation of these acids. Of the several methods that were under consideration, the one based on the fusion curve of mixtures of the corresponding sulfonamides was finally adopted. The melting points of these mixtures lie in a very convenient range of temperature, namely, 96.5° to 149.9°, and as will be seen from the curve, the eutectic point is sharply defined.

Preparation of Materials

Cymene-α-sulfonamide.—A mixture of one part of cymene with three parts of concd. sulfuric acid was heated on a water-bath maintained at 75°, and stirred by means of a mechanical stirrer until sulfonation was complete. The reaction product was dissolved in water, partially neutralized with barium hydroxide and finally with barium carbonate. The barium sulfate was filtered off, the filtrate concentrated on the steam-bath and subsequently allowed to crystallize. The first crop of crystals of barium cymenesulfonate thus obtained was thrice recrystallized from water and then converted into the sodium salt by means of sodium carbonate. The sodium cymenesulfonate was recrystallized from 95% alcohol and dried at 140°.

Fifty g. of sodium cymenesulfonate, 50 g. of phosphorus pentachloride and 10 cc. of phosphorus oxychloride were mixed in a mortar. A vigorous reaction took place immediately, and when it subsided the mixture was placed on the steam-bath for one-half hour. The product was then allowed to cool to room temperature and subsequently poured into ice water. The cymenesulfonyl chloride was extracted with ether and, after the evaporation of the ether, was obtained as a nearly colorless oil. An excess of aqueous ammonia was added to this, and the mixture heated by placing it at intervals on the steam-bath. When the very penetrating odor of the sulfonyl chloride had passed, the reaction was considered complete. The crude sulfonamide was filtered off and washed with cold water. The product was dissolved in hot water, the solution boiled with animal charcoal, and allowed to crystallize. The colorless crystals thus obtained were recrystallized from water a number of times until a product having a constant melting point was obtained.

Cymene-β-sulfonamide.—The sodium salt of cymene-β-sulfonic acid was prepared according to a method described in a previous paper.[9] The sulfonamide of this acid was prepared using exactly the same method described for the preparation of cymene-α-sulfonamide.

Determination of Fusion Points

The apparatus used for the determination of the fusion points was similar to that employed by McKie[10] for obtaining the melting-point curve of *o*- and *p*-toluenesulfonamides. The heating bath consisted of a large

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[9] THIS JOURNAL, **45**, 1489 (1923).

[10] McKie, *J. Chem. Soc.*, **113**, 799 (1918).

beaker filled with redistilled glycerol and provided with a thermometer and mechanical stirring device. The bath was heated with gas, the size of the flame being regulated by a screw clip compressing the rubber tubing. The sulfonamide was contained in a small test-tube fitted with a stirrer and an Anschütz thermometer, graduated to 0.2°, which had been standardized by the Bureau of Standards. This tube was enclosed in a larger one which was immersed in the glycerol bath. Sufficient material (1 to 1.5 g.) was used to cover the bulb of the thermometer completely with the molten mass. The whole apparatus was screened from drafts.

To determine the melting point of the substance, the temperature of the bath was raised to within 10° of the expected melting point. The temperature was subsequently increased slowly, and the temperature of the bath kept 1° above that recorded by the thermometer surrounded with the material. The melting point was taken as the lowest temperature at which a clear liquid was just obtained.

Determination of the Melting-Point Curve

The melting point of each pure isomer was first determined. Mixtures containing weighed amounts of the two components were made up and their melting points determined. The results obtained in these determinations are recorded in Table I and graphically in Fig. 1, in which the melting points are plotted against the percentage composition of the mixture.

TABLE I

MELTING POINTS OF THE TWO-COMPONENT SYSTEM OF THE α- AND β-SULFONAMIDES OF CYMENE

α, %	100	89.51	79.93	75.02	70.01	60.08	49.91	39.96	34.87	30.50	20.29	10.47	0	67.50
β, %	0	10.49	20.07	24.98	29.99	39.92	50.09	60.04	65.13	69.50	79.71	89.53	100	32.50
M. p., Corr. °C.	115.1	110.0	105.0	102.0	98.6	104.4	114.6	124.0	128.2	132.2	138.4	144.1	149.9	96.5

It will be noted that the melting-point curve is of the general type in which the two components do not unite to form an addition compound. The eutectic mixture contains 32.5% of the cymene-β-sulfonamide and 67.5% of the cymene-α-sulfonamide, and melts at 96.5°.

In applying this method for the determination of the relative amounts of cymene-α- and -β-sulfonic acids, in a sulfonation product, the question arose as to what effect the presence of cymene-disulfonic acid would have on the results. It is known that in the sulfonation of cymene, especially at higher temperatures, some disulfonic acid is formed. This acid, if present, would also give a sulfonamide which would be apt to affect the melting point of the mixture. The literature contained no information on the properties of the sulfonamide of cymene-disulfonic acid, particularly as to its solubility. This sulfonamide was therefore prepared and its properties studied. The following is a description of the method used in its preparation.

Cymene was treated with five times its weight of concd. sulfuric acid, the mixture stirred by means of a mechanical stirrer, and heated for four hours at 100°. The barium salts of the sulfonic acids were prepared and fractionally crystallized. The first fractions, consisting of the barium salt of cymene-α-sulfonic acid were discarded. The filtrate from this was concentrated and the barium cymene-disulfonate precipitated with absolute alcohol. This was filtered off, dissolved in a minimum amount of water, and reprecipitated with absolute alcohol. The product was filtered off and dried at 140°.

Analyses. Subs., 0.5000, 0.5000: $BaSO_4$, 0.2704, 0.2700. Calc. for $C_{10}H_{12}(SO_3)_2Ba$: Ba, 31.99. Found: 31.82, 31.77.

The barium salt was converted into the sodium salt by means of sodium carbonate. From this sodium salt (25 g.) the corresponding cymene-disulfonyl chloride was prepared following the method already described for the preparation of cymenemonosulfonyl chloride. The liquid sulfonyl chloride thus obtained was treated with an excess of aqueous ammonia and heated on the steam-bath; it dissolved giving a clear solution. When the solution was concentrated to a small volume and cooled, the sulfonamide of cymene-disulfonic acid separated. The product was filtered off, dissolved in hot water, the solution boiled with animal charcoal, filtered, and when the filtrate was allowed to crystallize, a colorless crystalline product was obtained, yield, 2.2 g. It was found to melt at 168.4° (corr.).

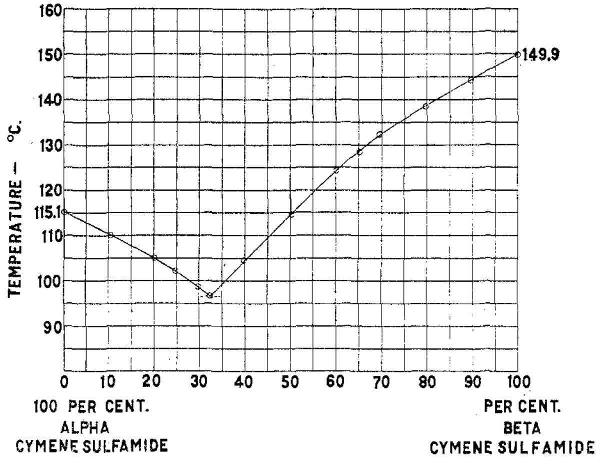

Fig. 1.

Analyses. Subs., 0.2026, 0.2043: 17.8 cc. of N_2 (30°, 766.4 mm.), 16.9 cc. (20°, 783.6 mm.). Subs., 0.1100, 0.1083: $BaSO_4$, 0.1759, 0.1736. Calc. for $C_{10}H_{12}(SO_2NH_2)_2$: N, 9.59; S, 21.93. Found: N, 9.75, 9.79; S, 22.02, 22.08.

In determining the solubility of the cymene-disulfonamide it was found to be very insoluble in ether, whereas the sulfonamides of cymene-α- and -β-monosulfonic acids are extremely soluble. One hundred g. of ether at 25° dissolves 0.0727 g. of the cymene-disulfonamide, or one part in 1375 parts by weight of ether. Accordingly, before making any determination of the melting point of a sulfonamide mixture obtained from the sulfonation product of cymene, it was dissolved in the minimum amount of ether and filtered to remove inorganic salts and cymene-disulfonamide, if present. The filtrate then contained only cymene-α- and -β-sulfonamides.

Sulfonation Experiments

The method used in carrying out the various sulfonation experiments may be briefly described as follows.

The sulfonator consisted of a long cylindrical vessel (the outer jacket of the so-called Dunbar Extractor was used for this purpose) provided with a mechanical stirring device, dropping funnel, thermometer and reflux condenser. This was placed either in a water- or glycerol-bath which was maintained at the desired temperature. The cymene and sulfuric acid were added from the dropping funnel and the stirring device was then set in motion. In the experiment conducted at 0°, both the cymene and sulfuric acid were first cooled to this temperature and then placed in the sulfonator which was surrounded with ice. When the sulfonation was complete, the product was dissolved in water, partially neutralized with barium hydroxide and subsequently with barium carbonate. The barium sulfate was filtered off and the filtrate concentrated. The first crop of crystals of the barium salt of α-cymene-monosulfonate was filtered off and the filtrate concentrated to a volume of about 100 cc. Absolute alcohol was added to this until all of the barium cymene-disulfonate was precipitated. This was filtered off, dried at 120°, weighed, and analyzed for barium. From the barium determinations the quantity of pure cymene-disulfonate was calculated. The alcoholic filtrate was evaporated to dryness on the steam-bath and the residue added to the barium salt of α-cymene-monosulfonate. This was dried at 120°, weighed, and subsequently converted into sodium salt by means of sodium carbonate. A 25g. sample of the sodium salt, dried at 140°, was converted into the sulfonyl chloride and subsequently into the sulfonamide, following the method already described. The mixture of crude sulfonamides thus obtained was dissolved in hot water, the solution boiled with animal charcoal, filtered, and the filtrate concentrated. The various fractions of sulfonamide crystals obtained were combined and dissolved in a minimum amount of ether and the ether solution filtered. The filtrate was evaporated to dryness on the steam-bath, the residue dried at 100°, and the melting point of the mixture of sulfonamides determined. A small amount of either pure α- or pure β- sulfonamide was then added to this and the melting point determined again. The percentage compositions corresponding to these melting points were then read from the curve.

The cymene used in these experiments was isolated from so-called sulfite turpentine and was specially purified by treatment with concd. sulfuric acid. It boiled at 177° to 177.6° (764.5 mm.) and produced only a faint coloration with sulfuric acid. Fifty g. of cymene was usually taken for each sulfonation experiment. However, in those experiments where a large excess of sulfuric acid was used, a smaller sample of cymene was taken, because of the limited capacity of the sulfonator.

Unless stated otherwise, it is to be understood that c. p. sulfuric acid of d. 1.84 was used.

The first series of sulfonation experiments was conducted at 100°, the sulfonation period being kept constant (four hours, preliminary experiments having indicated that sulfonation was complete in that time) but the ratio of sulfuric acid to cymene varied. The results obtained are recorded in Table II.

TABLE II

EFFECT OF VARIOUS AMOUNTS OF SULFURIC ACID AT THE SULFONATION TEMPERATURE OF 100°

Temperature, 100°. Sulfonation period, four hours

Expt.	$C_{10}H_{14}/H_2SO_4$	Cymene-disulfonic acid %	Cymene-α-sulfonic acid %	Cymene-β-sulfonic acid %	Cymene-β-sulfonic acid in sulfonation product %
1	1:2	0	87.5	12.5	12.5
2	1:3	5.4	83.5	16.5	15.6
3	1:4	5.4	85.0	15.0	14.2
4	1:5	8.1	84.2	15.8	14.5
5	1:6	9.8	84.6	15.4	13.9
6	1:7	10.5	85.2	14.8	13.2
7	1:8	12.1	84.6	15.4	13.5

These results indicate that the amount of cymene-β-sulfonic acid produced is not materially affected by the relative quantity of sulfuric acid used, although a ratio of cymene to sulfuric acid of 1:3 gives the best results. As would be expected, the percentage of disulfonic acid increases with the increased proportion of sulfuric acid to cymene. An increased yield of disulfonic acid in general produces a corresponding decrease in the yield of cymene-monosulfonic acids which, in turn, results in a decrease in the absolute amount of cymene-β-sulfonic acid produced.

Using the same period of sulfonation, namely, four hours, a similar series of experiments was carried out at the temperature of 75°. The results obtained are given in Table III.

TABLE III

EFFECT OF VARIOUS AMOUNTS OF SULFURIC ACID AT THE SULFONATION TEMPERATURE OF 75°

Temperature, 75°. Sulfonation period, four hours

Expt.	$C_{10}H_{14}/H_2SO_4$	Cymene-disulfonic acid %	Cymene-α-sulfonic acid %	Cymene-β-sulfonic acid %	Cymene-β-sulfonic acid in sulfonation product %
1	1:3	0.4	86.5	13.5	13.4
2	1:4	1.3	85.2	14.8	14.6
3	1:5	1.4	85.6	14.4	14.2
4	1:6	2.6	87.0	13.0	12.7
5	1:7	5.9	88.0	12.0	11.3
6	1:8	6.8	87.4	12.6	11.8
7	1:16	7.3	88.0	12.0	11.1

It is to be noted that, on the whole, the yields of cymene-β-sulfonic acid produced at 75° were somewhat less than those at 100°. With the increase in the ratio of sulfuric acid to cymene, a decrease in the yields of cymene-β-sulfonic acid was obtained due primarily to the greater proportion of cymene-disulfonic acid produced.

In order to study further the effect of temperature and concentration of sulfuric acid on the yield of cymene-β-sulfonic acid, a similar series of experiments was conducted at 50° and at 0°. In Expt. 7 (Table IV) fuming sulfuric acid (containing 20% of sulfur trioxide) was used, for it was found that at this temperature ordinary concd. sulfuric acid (d., 1.84) sulfonated cymene very slowly. Thus when one part of cymene and three parts of concd. sulfuric acid were stirred together for four hours at 0° only about 8% of the cymene was sulfonated. The results obtained are recorded in Table IV.

Table IV

Effect of Various Amounts of Sulfuric Acid at the Sulfonation Temperatures of 50° and 0°

Temperature, 50° except in Expt. No. 7, which was 0°. Sulfonation period, four hours. No cymene-disulfonic acid was obtained in any experiment

Expt.	$C_{10}H_{14}H_2SO_4$	Cymene-α-sulfonic acid in sulfonation product %	Cymene-β-sulfonic acid in sulfonation product %
1	1:3	90.0	10.0
2	1:4	89.0	11.0
3	1:5	89.0	11.0
4	1:6	89.0	11.0
5	1:7	89.2	10.8
6	1:8	87.4	12.6
7[a]	1:3	97.5	2.5

[a] Fuming sulfuric acid (20% SO_3) used in this experiment.

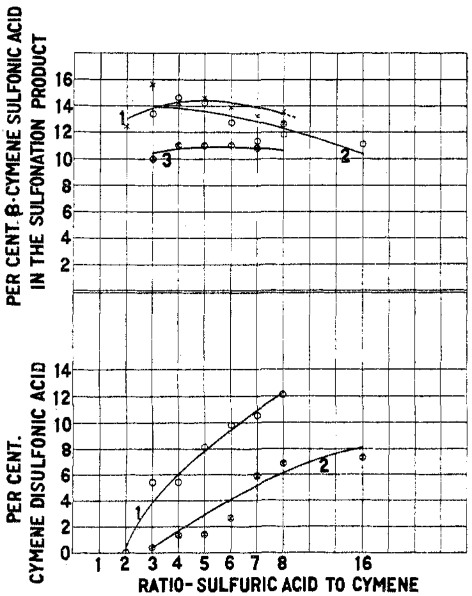

Fig. 2.—1. Temp. of sulfonation, 100°; 2. Temp. of sulfonation, 75°; 3. Temp. of sulfonation, 50°; sulfonation period, 4 hours.

These results show that the amount of sulfuric acid used has very little effect on the yield of cymene-β-sulfonic acid produced, whereas the temperature does have a marked effect. Thus the average percentage of β acid in the experiments conducted at 50° was 11%, whereas at 0° it was only 2.5%. The results obtained are shown graphically in Fig. 2.

Inasmuch as the results of the previous experiments indicated that large proportions of sulfuric acid were not particularly favorable to the production of greater yields of cymene-β-sulfonic acid and that temperature seemed to be the principal factor involved, experiments were, therefore, carried out at 125°, 150° and 175°, using a ratio of cymene to sulfuric acid of 1:2. In the experiment conducted at 175°, oxidation of the cymene took place rapidly, as was evident by the large amounts of sulfur dioxide given off. From the resultant sulfonation product, no crystalline sulfonamide could be obtained. The results of the experiments at 125° and at 150° are given in Table V.

TABLE V

EFFECT OF TEMPERATURE

Ratio $C_{10}H_{14}$:H_2SO_4 = 1:2. Sulfonation period, four hours

Expt.	Temp. °C.	Cymene-disulfonic acid %	Cymene-α-sulfonic acid %	Cymene-β-sulfonic acid %	Cymene-β sulfonic acid in sulfonation product %
1	125	14.3	85.2	14.8	12.7
2	150	19.8	90.0	10.0	8.0

It will be noted in Expt. 1 that although the relative amount of cymene-β-sulfonic acid produced was greater than that obtained at 100° under similar conditions (Expt. 1, Table II), nevertheless the yield of β acid when calculated as percentage of the total sulfonation product was practically the same as that at 100°, due to the fact that at 125° a considerable part (14.3%) of the total sulfonation product was disulfonic acid. In Expt. 2, however, a decrease in the yield of cymene-β-sulfonic acid was obtained so that, on the whole, it would seem that 100° is the optimum temperature for the production of the β acid when the ratio of cymene to sulfuric acid is 1:3.

Using the optimum conditions of temperature and concentration of sulfuric acid already determined, experiments were performed for the purpose of determining the effect of certain salts on the sulfonation of cymene. In each experiment 50 g. of cymene, 150 g. of sulfuric acid and 1 g. of the salt under investigation were used. The results obtained are recorded in Table VI.

TABLE VI

EFFECT OF THE ADDITION OF CERTAIN SALTS

Ratio, $C_{10}H_{14}$:H_2SO_4 = 1:3. Temperature, 100°. Sulfonation period, four hours

Sulfate added	K	Ag	Hg^{II}[a]	Cu^{II}[b]	CO^{II}	Ni^{II}
α acid, %	85.2	86.0	90.3	90.6	83.5	84.5
β acid, %	14.8	14.0	9.7	9.4	16.5	15.5

[a] Large amount of sulfur dioxide given off.

[b] Considerable amount of sulfur dioxide given off.

These results indicate that potassium, silver, cobaltous and nickelous sulfates have no effect on the relative amounts of cymene-α- and β-sulfonic acids produced. The slight differences between these results and that obtained under similar conditions when no salt was added (Expt. 2, Table II) are well within the experimental error. However, in the experiments where cupric and mercuric sulfates were used a considerable reduction in the yield of cymene-β-sulfonic acid was obtained. This may be due either to the fact that these salts catalyze the reaction so that more of the α acid is produced or that the β acid is less stable and more readily oxidized under these conditions than the α acid.

The writer wishes to take this opportunity to express his thanks to M. J. Goss of this Laboratory for his valuable aid rendered in connection with the experimental part of this work.

Summary and Conclusions

The melting-point curve of the two-component system of the α- and β-sulfonamides of cymene has been determined. Using this as a means of estimating the percentage composition of the reaction product of cymene and sulfuric acid, several series of experiments on the sulfonation of cymene under various conditions have been performed. The results indicate that temperature is the principal factor in determining the relative quantities of α- and β-sulfonic acids of cymene produced. The best yield (15.6%) of cymene-β-sulfonic acid was obtained at 100° when the ratio of cymene to sulfuric acid was 1:3, whereas, at 75°, 50° and 0° the yields were 13.4, 10.0 and 2.5, respectively. Temperatures above 100° were unfavorable to the production of cymene-β-sulfonic acid, due principally to the large proportion of disulfonic acid formed. The yield of cymene-β-sulfonic acid produced is not materially affected by the concentration of the sulfuric acid with respect to the cymene, although a large excess of acid gives a high yield of disulfonic acid which decreases the total quantity of cymene-monosulfonic acids obtained. The best proportion of cymene to sulfuric acid is 1:3. The yield of cymene-β-sulfonic acid is not affected by the addition of such salts as potassium, silver, cobaltous and nickelous sulfates to the cymene-sulfuric acid mixture. Cupric and mercuric sulfates, on the other hand, decrease the yield of cymene-β-sulfonic acid.

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