

Synthesis of Cresol

SULFONATION OF TOLUENE

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THE present work was carried out as part of a project to determine the economic feasibility of producing synthetic cresol. Although it is known that toluene can be sulfonated, little information is available on this subject (29). Most information about the sulfonation of toluene is found in the patent literature (1-3, 6-10, 20) as methods and processes for its manufacture, and often the sulfonation of toluene is added to the patents only in a general manner. About 65 patents were referred to in the original work, but those mentioned here are considered as the basic references to the sulfonation of toluene. The work of Holleman and Caland (19) carried out over 40 years ago apparently is still the major reference on this subject but it considered only the distribution of isomers at temperatures below 100° C.

The use of catalysts has been investigated by Holleman and Caland (19), Holdermann (18), and more recently by Hennion and Schimdle (17). Hennion and Schimdle (17) found that boron trifluoride had no directive influence on the yields obtained but it was possible to obtain cleaner yields at lower temperatures.

The patent literature with respect to the sulfonation of toluene is uniform in its appreciation of the fact that acid concentration is important. Ambler and Gibbs (1) described the use of a packed column for sulfonation at a temperature of 150° C. in which toluene vapors pass up the column and carry off the water of reaction while the sulfuric acid flows down the column and carries with it the toluenesulfonic acid. Carr, Dahlen, and Hitch (9) used sulfur dioxide as a diluent with sulfur trioxide as the sulfonating agent. Bender (3) described the use of vacuum to remove the water of reaction. Brown (?) removed the water of reaction by refluxing, and LeMaistre, Strickland, and Weaver (20), in one of the few specific patents on the synthesis of cresol, used a vapor feed to remove the water of reaction. No data are available on the effect of acid concentration. Furthermore, since the literature does not describe the effect of temperature, ratio of reactants, time of reaction, or comparative values using oleum instead of concentrated sulfuric acid, it was deemed advisable to fill this gap before studying the caustic fusion of sodium toluenesulfonate. It would then be possible to better evaluate the effect of the variables in sulfonation on the caustic fusion step.

EQUIPMENT

The sulfonation reactions were carried out in ground glass equipment. A 1-liter round-bottomed flask was fitted with a propeller-type mercury seal stirrer connected to a variable speed motor which could be controlled directly on the motor housing at about 600 r.p.m. One neck of the round-bottomed flask was fitted with a Claisson tube so that a thermometer could be inserted into the flask to measure the reaction temperature and was also fitted to a 500-ml. graduated separatory funnel for addition of the sulfuric acid at a known rate. The thermometer had a special 11-inch stem which almost touched the bottom of the flask. The second neck of the flask was fitted with a condenser for refluxing vapors or when the water of reaction was removed a special Bidwell receiver was added to provide a short settling period to ensure separation of water before the toluene was

returned to the flask. Heat was supplied to the flask through a Glas-Col heating mantle which was controlled through a Variac.

ANALYTICAL PROCEDURE

Analyses of samples were carried out to determine total toluenesulfonic acid, unreacted sulfuric acid, and *p*-toluenesulfonic acid. Water present in the samples was calculated and the quantity of toluene recovered was found by separation from the acid layer.

Unreacted sulfuric acid and total toluenesulfonic acid were determined by a method similar to that used by Harvey and Stegeman (16). The excess sulfuric acid was assumed to be the difference between the total acidity of the sample and the acid equivalent of the sulfuric acid in the sample.

Water in the acid product was calculated as the water of reaction plus the quantity of water in the sulfuric acid at the start of the run. Unreacted toluene was the least accurate determination, for it was found as recovered toluene in the separation of toluene from the acid layer. Some toluene was recovered initially on standing a short time and a small amount was recovered when water was added to the mixed acid prior to neutralization.

Determination of sulfuric acid as barium sulfate was found accurate to $\pm 0.5\%$ with known samples. Gravimetric determinations were found to be generally lower than titrimetric procedures for reasons amplified by Rieman and Neuss (26). Mixed acid samples were found to produce coarser precipitates of barium sulfate than those obtained from sulfuric acid alone, which made filtration of the precipitate easier than expected. Samples were run in triplicate and typical results are given in Table I. In general it was found that the weight per cent sulfuric acid reacted checked the per cent toluenesulfonic acid produced within $\pm 1\%$ as shown in Table I.

TABLE I. TYPICAL ANALYSIS FOR EXCESS SULFURIC ACID AND TOLUENESULFONIC ACID

Run	Excess H ₂ SO ₄ , %		H ₂ SO ₄ Reacted, %	Toluenesulfonic Acid Produced, %
21	33.23	33.21	33.05	66.77
22	14.96	15.12	14.95	85.02
27	39.23	39.13	39.21	60.79
28	38.23	38.15	37.24	61.85
30	54.73	54.63	54.33	45.67
33	28.25	28.22	27.95	72.05
34	10.35	10.08	10.08	89.92
38	38.54	38.83	38.85	61.15
40	36.65	36.85	36.80	63.35
44	49.14	49.16	49.03	50.84
49	18.57	18.44	18.69	81.56
50	30.67	30.55	30.54	69.46
51	50.52	50.68	50.67	49.48
52	43.73	43.88	43.80	56.27
66	40.38	40.50	40.50	59.50

Formation of sulfones was considered negligible in all runs carried out at temperatures below 150° C. Harvey and Stegeman (16) and Othmer and Leyes (23) in their work on sulfonation of benzene discounted the presence of sulfone because of the absence of insolubles in the product obtained. Samples in the present work were found to be clear and no insolubles were found even after the material had been concentrated.

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Determination of *p*-toluenesulfonic acid was carried out by the procedure of Holleman and Caland (19) in which toluenesulfonic acid or its salt is converted to toluenesulfonyl chloride by reaction with phosphorus pentachloride. The freezing point of toluenesulfonyl chloride is determined and the per cent para isomer obtained from the freezing point curve. Melting point data from Harding (14, 15) were also used to check samples. These curves are shown in Figure 1.

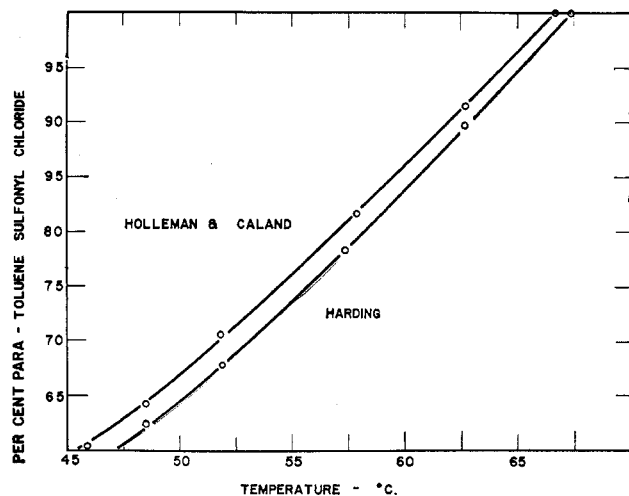


Figure 1. Melting and Freezing Point Curves for the System *o*-Toluenesulfonyl Chloride-*p*-Toluenesulfonyl Chloride

Briefly the analytical procedure was to mix 30 grams of sodium toluenesulfonate with 20 grams of phosphorous pentachloride. The mixture was placed in a large test tube in an oil bath at 130° C. for 1 hour and then poured into 200 ml. of ice water. The toluenesulfonyl chloride was taken up in ethyl ether, washed with additional ice water, and filtered. The ethyl ether was

evaporated, leaving a clean white crystalline product used for the melting point determination.

The effect of water used in washing samples of toluenesulfonyl chloride was found to be negligible. A sample whose melting point had previously been determined was placed in a test tube with water and allowed to stand for 1 week before drying and redetermination of the melting point. Difference in melting point was found to be in the order of $\pm 0.1^\circ$ C. for several samples.

Freezing point determination of the para isomer in a mixture of the three isomers was found to be reasonably accurate by Holleman and Caland (19), who established the similarity of curves for para-ortho and para-meta isomers. No satisfactory method of determining percentages of *o*- and *m*-toluenesulfonic acid was found in the literature.

DISCUSSION OF EXPERIMENTAL DATA

TIME AND TEMPERATURE. Initially a study was made to determine the effect of time and temperature using a 1 to 1 mole ratio of toluene and 96% sulfuric acid in which the acid was added to the toluene over a fixed period of time. Holleman and Caland (19) had indicated the effect of temperature on isomer distribution but did not show the effect of time or over-all conversion.

The 96% sulfuric acid was added to the toluene over an arbitrary time of 1½ hours which was selected solely to permit better control of the exothermic reaction at low temperatures. The data are tabulated in Table II and shown in Figures 2, 3, and 4. The figures were prepared with constant temperature lines. The ratios shown in all figures are mole ratios and "time acid added" refers to the total time of sulfuric acid addition.

In Figure 2 it will be noted that at 25° C. time has little effect on the yield of toluenesulfonic acid. As the temperature is increased the rate of reaction is also increased but finally, when the reaction is carried out at total reflux, the effect of time is less important than a new factor—acid concentration. It is known that as the sulfuric acid used in sulfonation becomes more dilute the rate of reaction will decrease. This is mentioned by Groggins (13) and others. The effect of acid concentration

is shown best where the water of reaction is removed by refluxing with toluene. Here the reaction rate is not limited until 90% of the reaction is complete and then because there was insufficient toluene left to continue refluxing. In no case was an absolute limiting acid concentration reached, as is shown in Figure 3. The use of excess toluene was studied in another group of runs.

Figure 4 shows that as the temperature of reaction was increased the conversion to the para isomer also increased to a maximum at 100° C. The effect of time was negligible. At total reflux and reflux with removal of water the para isomer content was found to be about 83 to 84%. In Table III a comparison is shown for para isomer distribution at various temperatures for the works of Holleman and Caland (19), Harding (14), and the authors. The present data cross the data of Harding (14) but are higher than the data of Holleman and Caland (19).

TABLE II. EFFECT OF TIME AND TEMPERATURE

(Mole ratio of reactants, 1 to 1; time of acid addition, 1½ hours)

Run	Temp., °C.	Total Time, Hr.	Wt. % Excess Sulfuric Acid	Wt. % Toluene-sulfonic Acid	Acid Concn., %	Wt. % Toluene Recovered	Yield, % (Toluene-Free Basis)				Para Isomer, %
							Toluene-sulfonic acid	Sulfuric acid	Water	Unaccounted for	
4	25	2	64.11	34.00	85.64	68.13	43.99	47.97	8.04
2	25	3	65.73	34.04	86.27	66.87	43.18	48.61	7.56	0.65	70.8
3	25	4	65.01	34.23	85.99	66.87	43.61	48.13	7.86	0.40	70.6
5	25	5	63.65	36.63	85.64	63.75	45.68	45.91	7.81	0.60	71.7
29	25	8	65.18	35.22	86.55	65.63	44.30	48.30	7.40	..	78.0
6	50	2	61.56	33.77	85.64	64.78	48.30	43.50	7.35	0.85	..
35	50	2	62.69	36.17	85.49	61.25	44.60	44.93	7.58	2.89	78.0
7	50	3	59.51	40.49	83.69	60.00	49.62	42.17	8.21	..	79.2
8	50	4	57.79	41.33	83.98	58.49	50.87	40.83	8.30
8a	50	4	57.92	42.35	83.70	56.60	51.85	40.38	7.77	..	79.2
13	50	5	56.62	42.56	83.13	59.50	52.38	39.16	8.46	..	80.0
30	50	8	54.33	43.95	81.78	56.40	52.60	37.66	8.38	1.36	78.0
9	75	2	52.66	46.20	81.49	47.50	55.47	36.29	8.24	..	79.1
10	75	3	49.51	47.64	79.80	50.31	57.13	33.82	9.05	..	80.8
11	75	4	47.09	50.22	78.40	44.30	59.00	31.76	9.24	..	80.0
12	75	5	43.16	55.02	76.10	44.02	62.83	28.29	8.88	..	82.1
31	75	8	43.03	57.28	75.21	42.50	63.16	27.57	9.08	0.19	..
17	100	2	41.94	58.41	75.08	44.10	64.27	26.49	9.24	..	83.1
16	100	3	38.44	61.70	72.29	40.56	66.77	23.70	9.53
27	100	3	39.21	62.81	72.91	28.75	65.00	23.46	8.60	2.94	84.6
28	100	3	38.15	61.60	71.73	33.33	65.27	23.23	9.16	2.34	84.3
15	100	4	36.13	63.52	71.51	39.85	68.26	22.12	9.62	..	86.6
14	100	5	34.75	65.71	69.27	38.40	69.39	20.90	9.71
32	100	8	32.21	69.69	66.59	24.06	69.08	18.55	9.30	3.07	85.3
21	2	3	37.94	62.93	70.92	37.13	66.80	23.10	9.55	0.55	84.3
24	3	3	33.37	69.84	67.10	17.50	68.00	18.79	9.22	3.99	81.7
25	4	3	33.51	68.50	67.21	27.60	68.92	19.49	9.52	2.07	82.5
23	4	3	31.87	69.72	65.68	27.60	69.52	18.37	9.60	2.51	83.2
26	5	3	30.67	71.62	64.50	24.50	71.59	17.80	9.82	0.79	83.7
33	5	3	27.95	72.00	62.26	18.13	70.95	16.00	9.70	3.35	83.0
19	2	2	30.48	70.88	69.16	23.75	71.52	17.78	7.93	2.77	84.0
45	2	2	29.66	71.05	73.12	25.50	74.16	18.00	6.61	1.23	83.7
18	3	3	22.54	78.82	65.18	9.27	76.98	12.73	6.79	3.50	84.6
22	4	3	14.98	85.79	59.76	..	81.69	8.25	5.55	4.51	82.1
47	4	3	10.49	91.50	51.01	3.12	87.22	5.75	5.89	1.51	84.6
34	8	3	10.08	90.80	53.96	..	85.67	5.53	4.71	4.09	83.0

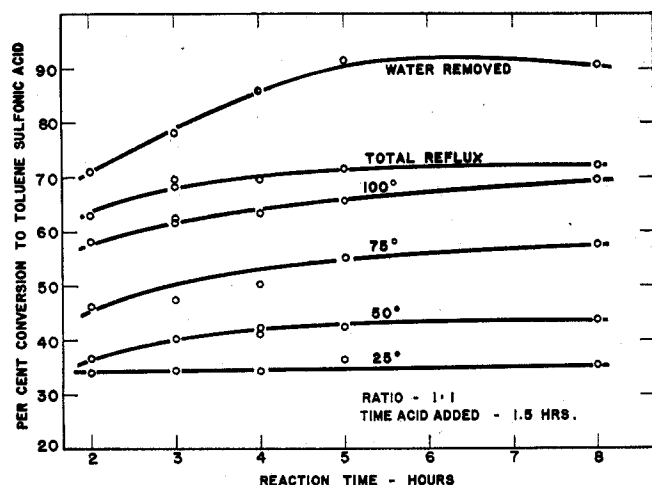


Figure 2. Effect of Time and Temperature of Sulfonation on Conversion to Toluenesulfonic Acid

TABLE III. EFFECT OF TEMPERATURE ON ISOMER DISTRIBUTION

Temp., ° C.	<i>p</i> -Toluenesulfonic Acid, %		Authors
	Holleman and Caland (19)	Harding (14)	
25		76.5	78.0
35	62.0
50	78.0
75	72.1	94.5	81.0
100	78.7	..	85.3
Reflux	83.0
H ₂ O off	83.0

The product obtained at 25° C. was an amber liquid while the product obtained at temperatures over 50° C. partially crystallized on cooling because of the sulfonic acid present. In no case was any insoluble material noted nor was the product darker than a light brown color.

This series of runs showed that the best yields could be obtained where the water of reaction was removed and that the yield of *p*-toluenesulfonic acid would be about 83 to 84%. It was also noted that although the product contained less than 6% free sulfuric acid the sulfuric acid concentration of 52 to 54% represents a potential corrosion problem. Since the sulfuric acid cannot be economically recovered for re-use and must therefore be neutralized, the most economical operation will be the one in which maximum conversion is effected.

VARIATION OF TIME OF ACID ADDITION. In the previous series of runs the sulfuric acid was added to the toluene over a period of 1½ hours. Since the type of curve obtained at 100° C. was representative of the curves obtained at the lower temperatures, all succeeding runs were carried out at 100° C. and also at reflux with removal of water which seemed to be an optimum operating condition. In this set of runs the time of acid addition was varied and the results are shown in Figures 5 and 6.

At 100° C. it was found that if the acid was added too quickly the exothermic reaction could not be controlled very easily and only the use of a condenser prevented the loss of toluene. When the acid was added over a period of ½ hour the reaction proceeded smoothly. Results show that the same yields can be obtained in less time when the acid is added in a shorter period.

In those runs in which the water of reaction was removed it was again apparent that the total reaction time could be reduced by adding the sulfuric acid in as short a time as possible while still being able to control the reaction mass. The results are shown in Figure 6.

Time of acid addition did not affect the conversion to *p*-toluenesulfonic acid. At 100° C. about 84 to 85% para isomer was formed and at reflux with removal of water about 83 to 84% para isomer was formed. The acid concentrations at the end of the runs were comparable, based upon the yield of toluenesul-

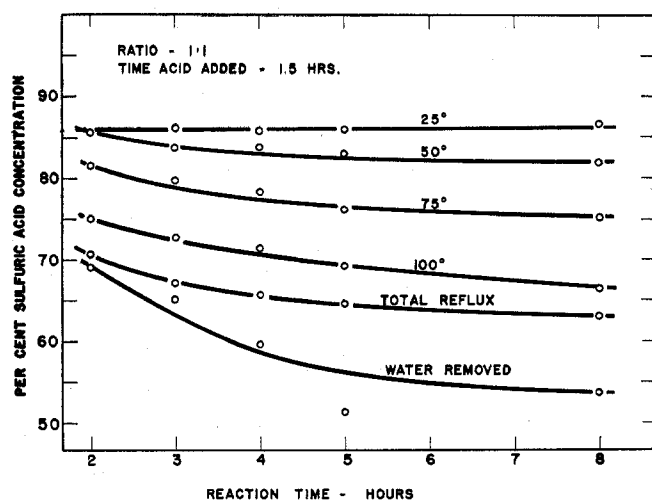


Figure 3. Effect of Time and Temperature of Sulfonation on Sulfuric Acid Concentration at End of Run

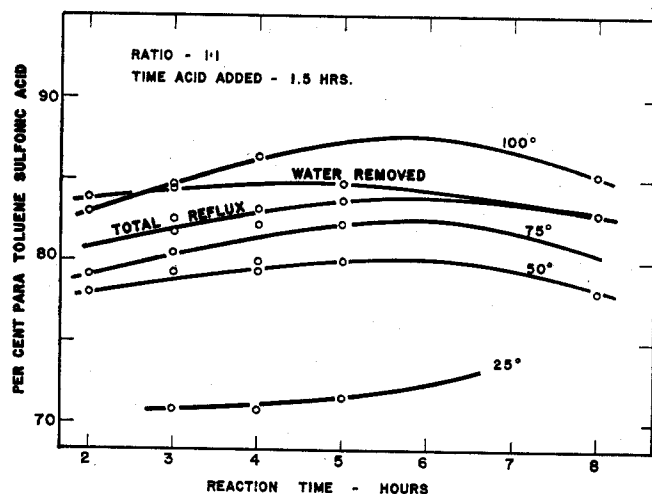


Figure 4. Effect of Time and Temperature of Sulfonation on Yield of *p*-Toluenesulfonic Acid

fonic acid. This set of runs indicates that the yield of toluenesulfonic acid is not appreciably affected by the time of acid addition. The rate of acid addition is only limited by the means available to control the exothermic reaction.

VARIATION OF RATIO OF REACTANTS. Previously it was noted that at reflux with removal of water the temperature in the flask will rise with constant heat input when the quantity of toluene available for refluxing decreases. In this set of runs the mole ratio of toluene and 96% sulfuric acid was varied in runs carried out at 100° C. and where water of reaction was removed. The results are shown in Figures 7 and 8. The time of acid addition was 1½ hours and the total reaction time was 3 hours. Figure 7 shows that as increased quantities of sulfuric acid were used the conversion to toluenesulfonic acid increased until almost 100% conversion was obtained when a 2 to 1 mole ratio of acid to toluene was used. While the conversion to sulfonic acid was increasing, the yield in the mixed acid product on a toluene-free basis decreased. Definition of the terms "yield" and "conversion" will explain this difference. Conversion refers to the per cent toluenesulfonic acid obtained based on the theoretical amount obtainable. Similarly, yield is the per cent toluene sulfonic acid in the mixed acid layer, on a toluene-free basis. Therefore it is possible to have 100% conversion where an excess of sulfuric acid is used but the yield can be low because the excess sulfuric acid is present in the mixed acid layer.

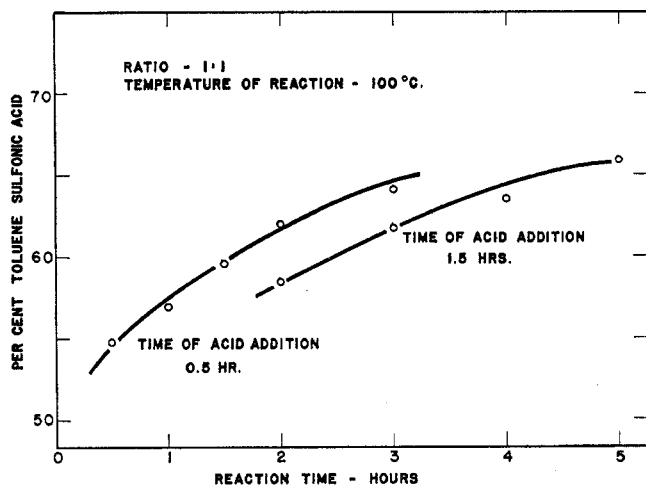


Figure 5. Effect of Time of Acid Addition during Sulfonation on Conversion to Toluenesulfonic Acid

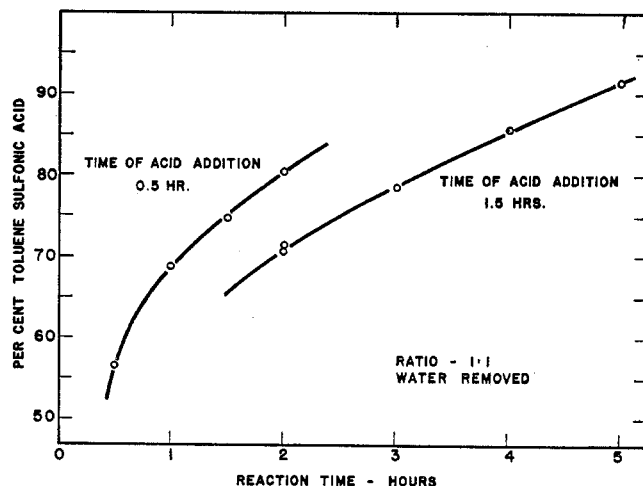


Figure 6. Effect of Time of Acid Addition during Sulfonation on Conversion to Toluenesulfonic Acid

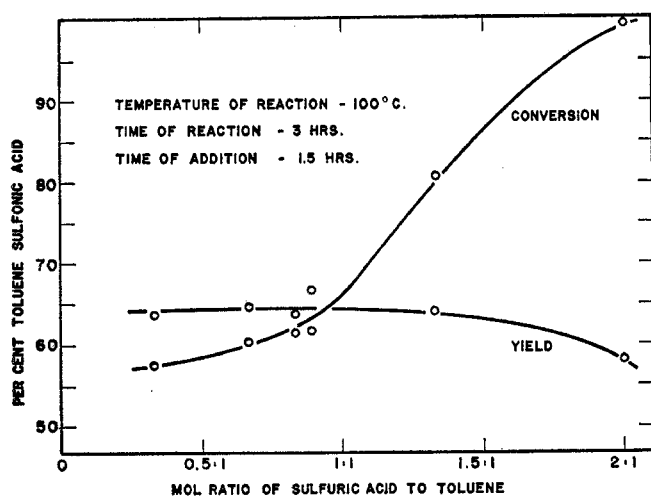


Figure 7. Effect of Varying Ratio of Reactants during Sulfonation on Conversion to Toluenesulfonic Acid

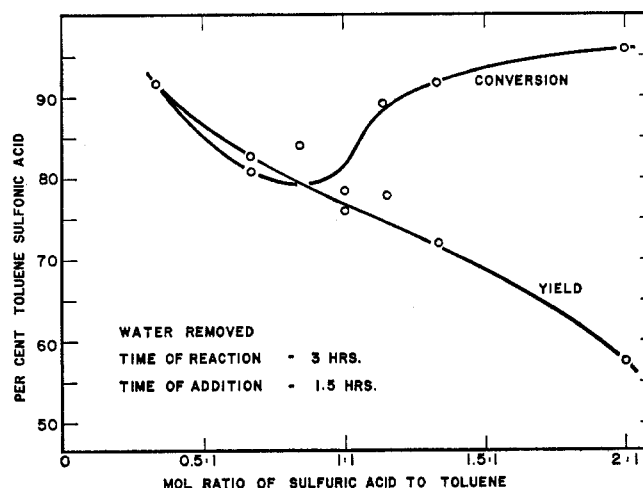


Figure 8. Effect of Varying Ratio of Reactants during Sulfonation on Conversion to Toluenesulfonic Acid

As previously noted, from an economic standpoint it is desirable to have a minimum quantity of free sulfuric acid present at the completion of a run because the excess acid must be neutralized. In those runs at 100° C. the conversion to the para isomer remained constant between 84 to 85% and the final sulfuric acid concentration was about 73%.

In those runs where the water of reaction was removed and where an excess of toluene was used both conversion and yield were high. The excess toluene helped to remove the water of reaction, thus driving the reaction to completion. A yield of 92% was obtained in the mixed acid layer where 100% excess toluene was used. As the quantity of excess toluene was reduced

both conversion and yield decreased to a minimum at a 1 to 1 mole ratio of reactants. Then as more and more sulfuric acid was used the conversion to sulfonic acid increased but the yield of sulfonic acid in the mixed acid layer decreased. The para isomer yield was found to be about 83% and the final sulfuric acid concentration for the set of runs varied from 66 to 69%.

The conclusion reached in this set of runs is that improved yields can be obtained where the water of reaction is removed with the use of excess toluene. The yield of para isomer is not affected by a change in the ratio of reactants. The final acid concentration will be about 66 to 69%.

VARIATION OF FINAL TEMPERATURE. The effect of increasing the reaction temperature using a 1 to 1 mole ratio of reactants

TABLE IV. EFFECT OF VARIATION OF FINAL TEMPERATURE

(Time of acid addition, 1/2 hour; time at max. temp., 1/2 hour; ratio of reactants, 1 to 1)

Run	Temp., ° C.	Total Time, Hr.	Wt. % Excess Sulfuric Acid	Wt. % Toluene- sulfonic Acid	Acid Concn., %	Wt. % Toluene Recovered	Yield. % (Toluene-Free Basis)					Para Isomer, %
							Toluene- sulfonic acid	Sulfuric acid	Water	Unaccounted for	Solids	
61	120	2	22.79	80.58	69.19	9.35	77.73	12.65	5.63	4.19	0.0	84.6
70	150	3 1/2	8.63	91.16	80.17	0.00	87.76	4.88	3.23	4.13	0.0	84.6
72	200	3 1/2	12.73	80.65	92.51	0.00	80.65	7.44	1.16	2.57	8.2	
71	180	3 1/2	9.38	89.29	72.13	0.00	88.08	5.40	2.08	3.33	1.1	7.80
73 ^a	225	3 1/4	12.55	46.83	...	4.5	52.52	7.95	39.5	...

^a Run 73 at 225° C. decomposed rapidly after a few minutes at this temperature and both water and toluene were collected in the Bidwell receiver.

TABLE V. COMPARISON RUNS BETWEEN OLEUM AND SULFURIC ACID
(Mole ratio of reactants, 1 to 1; time of acid addition, 1/2 hour)

Run	Temp., ° C.	Total Time, Hr.	Agent	Wt. % Excess Sulfuric Acid	Wt. % Toluene- sulfonic Acid	Acid Concn., %	Wt. % Toluene Recovered	Yield, % (Toluene-Free Basis)				Para Isomer, %
								Toluene- sulfonic acid	Sulfuric acid	Water	Unaccounted for	
69	100	2	Acid	38.13	62.05	72.37	32.5	63.57	22.81	8.71	4.81	83.2
75	100	2	Oleum	23.76	76.89	67.87	17.5	77.29	13.69	6.48	2.54	79.0
56	H ₂ O off	1	Acid	34.19	68.62	72.82	13.13	65.87	18.88	7.05	8.20	82.3
77	H ₂ O off	1	Oleum	19.66	79.10	68.65	15.0	80.66	11.49	5.25	2.60	78.3
61	H ₂ O off	2	Acid	22.79	80.58	69.19	9.35	77.73	12.65	5.63	4.19	84.6
76	H ₂ O off	2	Oleum	9.00	90.80	59.64	6.25	89.64	5.09	3.45	1.82	78.2

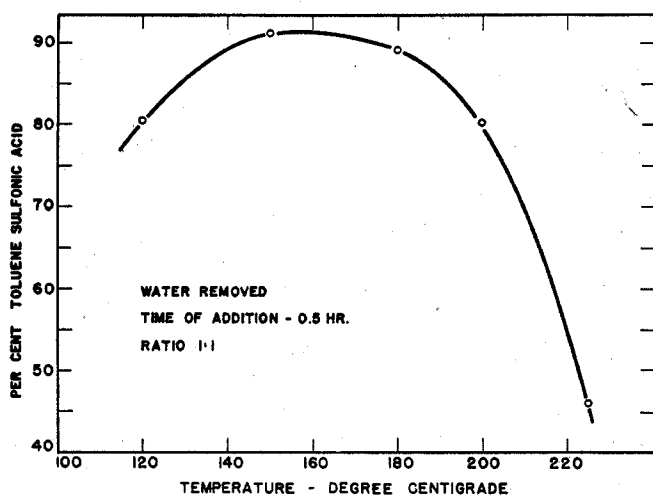


Figure 9. Effect of Varying Final Reaction Temperature during Sulfonation on Conversion to Toluenesulfonic Acid

after refluxing has ceased is given in Table IV and shown in Figure 9. The 96% sulfuric acid was added to the toluene in 1/2 hour and the reaction run up to the final reaction temperature with refluxing and constant heat input, at which time the reaction temperature was held constant for 1/2 hour by controlling the heat input.

The results show that 91% conversion could be obtained at 150° C. At temperatures over 150° C. the reaction mass turned black and increasing quantities of insoluble materials were formed. Finally at 225° C. the reaction mass began to decompose shortly after the temperature had been reached, with both water and toluene being given off. At the higher temperatures the

(Synthesis of Cresol)

CAUSTIC FUSION OF TOLUENESULFONIC ACID

THE preparation of synthetic cresol from toluene is essentially a two-step operation: (1) the preparation of a toluenesulfonate and (2) the hydrolysis of the sulfonate to cresol. After the toluenesulfonic acid had been analyzed it was neutralized with sodium hydroxide until it was just alkaline to phenolphthalein and then evaporated to facilitate storage until such a time as the fusion step could be carried out.

Some difference exists in the literature as to whether or not sodium hydroxide can be used in the caustic fusion of sodium toluenesulfonate. Gilman (12) states that sodium toluenesulfonate cannot be fused with sodium hydroxide and in order to carry out this fusion it is necessary to use a minimum of 28% potassium hydroxide in a mixture with sodium hydroxide. Mares (21) proposed to use a mixture of sodium benzenesulfonate and sodium toluenesulfonate in sodium hydroxide to carry out the

final sulfuric acid concentration was found to increase to 92%. Also, the per cent para isomer decreased as the temperature was increased and in the section on caustic fusion the increase was largely the meta isomer. Based upon the yields obtained it was found that the maximum yields are obtained at temperatures below 150° C.

OLEUM VERSUS 96% SULFURIC ACID. Several runs were carried out in which 15% oleum was added to the toluene over a period of 1/2 hour. The results of these runs compared to the results obtained with 96% sulfuric acid are given in Table V. The use of oleum improved the yields from 12 to 15% but the yield of para isomer decreased about 6% where oleum was used. The final sulfuric acid concentration where oleum was used as the sulfonating agent was comparable to the results from the use of 96% sulfuric acid where the yields of toluenesulfonic acid were the same. Subsequent work showed that the material from the oleum runs frothed during the caustic fusion step and as a result the over-all yield of cresol was reduced.

SUMMARY

Based upon the data obtained it was found that the best results were produced where 96% sulfuric acid was added to the toluene in the shortest possible time while still being able to control the reaction and where the water of reaction was removed with excess toluene. These results were enhanced where the final reaction temperature was held below 150° C. In this manner yields of 92 to 95% toluenesulfonic acid can be obtained containing about 84% *p*-toluenesulfonic acid.

Low reaction temperatures increased the yield of meta-ortho isomers as did reaction temperatures over 150° C. The over-all yield of these isomers was never over 25%. The use of oleum increases the yield of meta-ortho isomer to about 22% but frothing occurs during the fusion step.

fusion step. On the other hand, Bouvier and Bardin (5) make no mention of any difficulty in using sodium hydroxide in the fusion step. Tyrer (30) proposed the addition of either sodium or potassium sulfite or sulfate to act as an antifoaming agent during fusion. Similarly, LeMaistre, Strickland, and Weaver (20) carried out the fusion of sodium toluenesulfonate without difficulty and obtained a yield of 70% cresol.

In the present work the use of sodium hydroxide in the fusion step was investigated and compared with the results obtained using potassium hydroxide. It should be remembered that all samples in the fusion run contained varying amounts of sodium sulfate from the neutralization of the unreacted sulfuric acid in the sulfonation runs.

The equipment used for the caustic fusion of sodium toluenesulfonate consisted of an iron fusion pot 3 inches in diameter and