

## ON THE MECHANISM OF SULFONATION OF THE AROMATIC NUCLEUS AND SULFONE FORMATION

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Although sulfonations of aromatic hydrocarbons date back to near the beginning of modern organic chemistry, little had been published on the mechanisms of these reactions prior to the publication on this subject by Michael and Weiner in 1936 (1). The advent of stabilized sulfur trioxide on a commercial scale has increased the importance of the reactions of this material (2-4).

In a recent article (5), Leierson, Bost, and LeBaron presented their findings on the sulfur trioxide sulfonation of benzene in liquid sulfur dioxide to yield benzenesulfonic acid as the main product and lesser amounts of diphenylsulfone. These workers reported that the amount of diphenylsulfone formed, when the reaction was carried out at  $-8^{\circ}$ , near the boiling point of liquid sulfur dioxide, was dependent upon one or more of three factors:

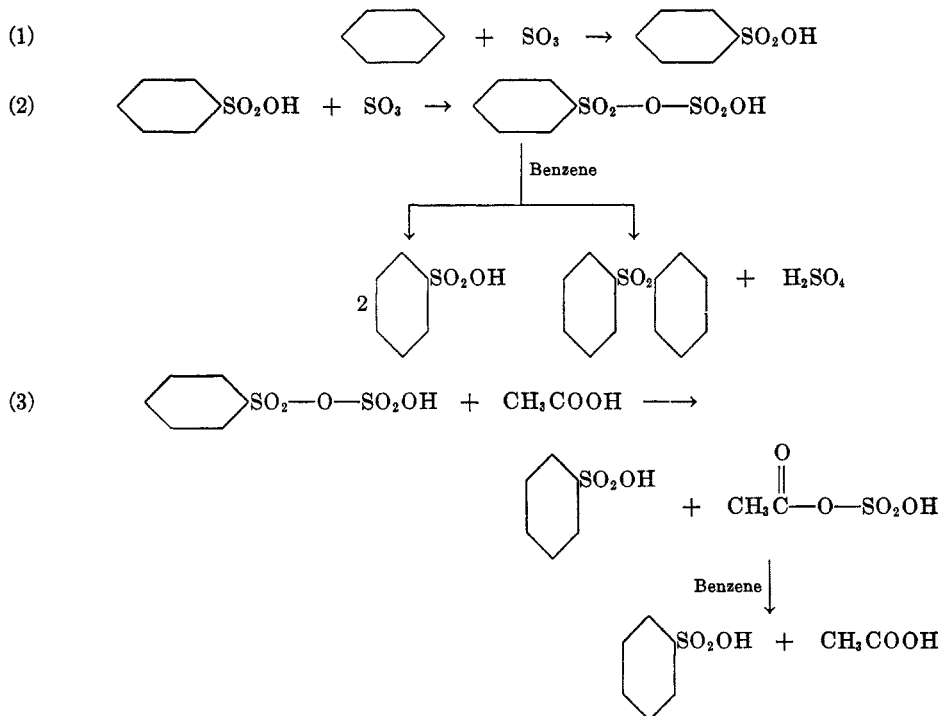
- (a) The order of addition of benzene and sulfur trioxide to liquid sulfur dioxide,
- (b) the warming of the reaction mixture after mixing of the reagents from  $-8^{\circ}$  to room temperature with accompanying expulsion of sulfur dioxide, and
- (c) the purity of benzene.

We have re-examined the reaction of benzene with sulfur trioxide in liquid sulfur dioxide and have found that the extent of concomitant sulfone formation is not dependent upon the purity of benzene to a significant degree as claimed by Leierson, Bost, and LeBaron. Instead, the percentages of sulfone in the reaction product were found to be dependent chiefly on the temperature of reaction and, especially, on the mole ratio of benzene to sulfur trioxide at various stages of the synthesis, when the hydrocarbon is added to the sulfur dioxide solution of sulfur trioxide.

Furthermore, it was found that carboxylic acids, present in the sulfonation medium even in small amounts, exercise a profound effect on sulfone formation; that is, their presence remarkably lowers the percentages of sulfone in the product as compared with the results obtained in their absence. Suter (6) states that the presence of carboxylic groups influences the sulfonation in the aromatic series because the sulfonating agent is more soluble in carboxylic acids and because the formation of a mixed anhydride or an addition compound may occur as the first step in the reaction. Our results confirm these ideas.

These combined findings led to the conclusion that pyrosulfonic acids are, in all probability, formed in the reaction of the aromatic hydrocarbon with sulfur trioxide and that these pyrosulfonic acids, through further reaction with benzene, are precursors to sulfones. In principle, at least, this concept agrees with that of Michael and Weiner (1). In our opinion, carboxylic acids react readily

with benzenepysulfonic acid to yield benzenesulfonic acid and acylsulfuric acid. When acetic acid is used, acetylsulfuric acid is formed which, although being generally recognized as a sulfonating agent, is not, by our mechanism, capable of sulfone formation. The reactions accompanying the sulfonation of benzene can be represented as follows, using acetic acid to illustrate the behavior of carboxylic acids generally:



Adding one mole of benzene slowly under the surface of a solution of 1.05<sup>1</sup> moles of sulfur trioxide in 500 ml. of liquid sulfur dioxide in 10 to 15 minutes at  $-9^\circ$ , followed by heating the reaction mass to  $65^\circ$  for 20 minutes results in a sulfonated product containing 6.5% diphenylsulfone. Adding 1.8 g. of glacial acetic acid to the  $\text{SO}_2\text{—SO}_3$  mixture prior to the addition of benzene reduces the sulfone content to 1% or less. However, adding all of the benzene at  $-9^\circ$  to the  $\text{SO}_2\text{—SO}_3$  mixture results in troublesome handling of the product upon evaporating and expelling sulfur dioxide. The reaction product begins to solidify at about  $-4^\circ$  and has to be heated to  $45\text{--}75^\circ$  to obtain a homogeneous anhydrous, liquid product from which all but a trace of sulfur dioxide has been removed.

During the course of our studies we observed that when one-half mole of benzene is allowed to react with 1.00 to 1.05 moles of sulfur trioxide in 500 ml. of sulfur dioxide, there results a product which remains liquid at all temperatures from  $-9^\circ$  to  $60^\circ$ , even after expulsion of sulfur dioxide at  $-4^\circ$  to  $10^\circ$ . This prod-

<sup>1</sup> A slight excess of  $\text{SO}_3$  over 1.00 mole is used here to allow for losses of this magnitude found to occur along with  $\text{SO}_2$  evaporation.

uct undoubtedly contains benzenepyrosulfonic acid which reacts with more benzene after sulfur dioxide removal to yield both benzenesulfonic acid and diphenylsulfone. It is, therefore, possible to add the second half mole of benzene at any given temperature between  $-9^{\circ}$  and the practical upper temperature limit of  $75^{\circ}$ .

After the second addition of benzene to the pyrosulfonic acid at  $10^{\circ}$ , the temperature rises rapidly to  $85-90^{\circ}$  followed by a temperature decline. In order to maintain any given reaction temperature above  $10^{\circ}$ , external cooling or heating must be applied, as needed. A reaction period of 20 minutes at a given temperature was found to be sufficient for essential completeness with air being drawn over the product during the last five minutes to remove remaining sulfur dioxide.

The results of a series of experiments utilizing this procedure are given in Table I and, graphically, in Figure 1.

It should be pointed out that the initial reaction of benzene with sulfur trioxide is very vigorous. However, in the two stage sulfonation, the addition of 0.5 mole of benzene, in the second step, to 0.5 mole of pyrosulfonic acid at  $10^{\circ}$  does not take place nearly so vigorously. As a matter of fact, the second 0.5 mole of benzene can be added to the pyrosulfonic acid at  $10^{\circ}$  very rapidly with an  $80$  to  $85^{\circ}$  attendant rise in temperature. This fact in itself supports the pyrosulfonic acid concept since the excess sulfur trioxide combined with benzenesulfonic acid as the pyro acid has been noticeably reduced in its energy.

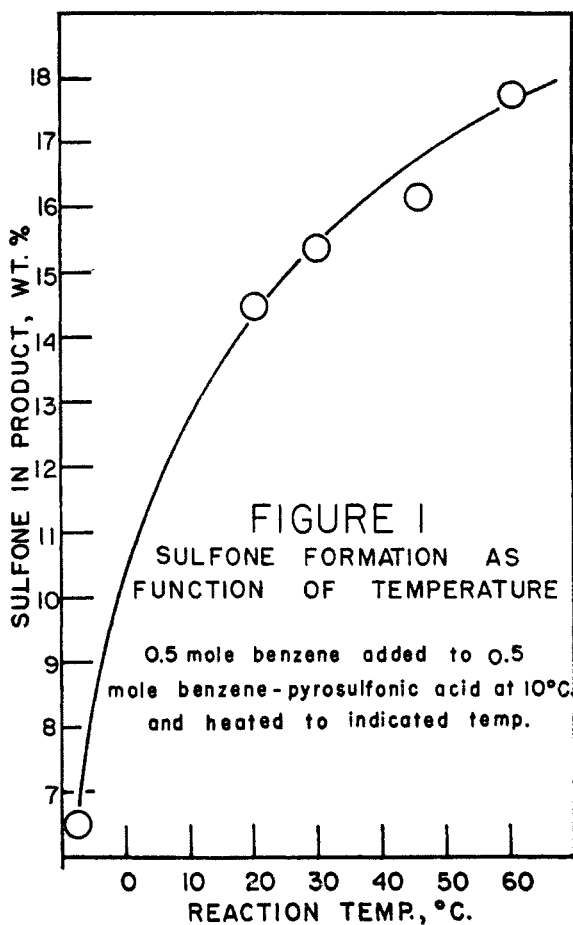
The effect of acetic acid on the path of sulfonation was noted in separate experiments performed under identical conditions except that 1% glacial acetic acid based on the combined weight of hydrocarbon and sulfur trioxide was added to the  $\text{SO}_2\text{-SO}_3$  mixture. Also, the reaction temperatures were allowed to rise freely to  $90^{\circ}$  after the second benzene addition. Two minutes after the maximum

TABLE I  
SULFONE FORMATION RESULTING FROM THE ADDITION OF BENZENE TO  
BENZENEPYROSULFONIC ACID AT VARIOUS TEMPERATURES

(0.5 mole of benzene added to 0.5 mole of benzenepyrosulfonic acid at  $10^{\circ}$ . Reaction mixture stirred for 20 minutes at indicated reaction temperatures with air sweeping over reaction product during last 5 minutes)

Reaction Temperature, $^{\circ}\text{C}$ .	Sulfone in Product, weight-%	Remarks
$-9^{\circ}$	6.52	Product solid at $-4^{\circ}$ . Heated to $60^{\circ}$ to obtain homogeneous liquid.
20	14.52	Product solidified
30	15.40	Semi-liquid product
45	16.20	Liquid product
60	17.85	Liquid product
75	18.28	Liquid product

\* All of the benzene was added at  $-9^{\circ}$  in this run. In all remaining runs one-half of the benzene was added at  $-9^{\circ}$  and the second half at  $10^{\circ}$ . Reaction temperatures were maintained by external heating or cooling, as needed.



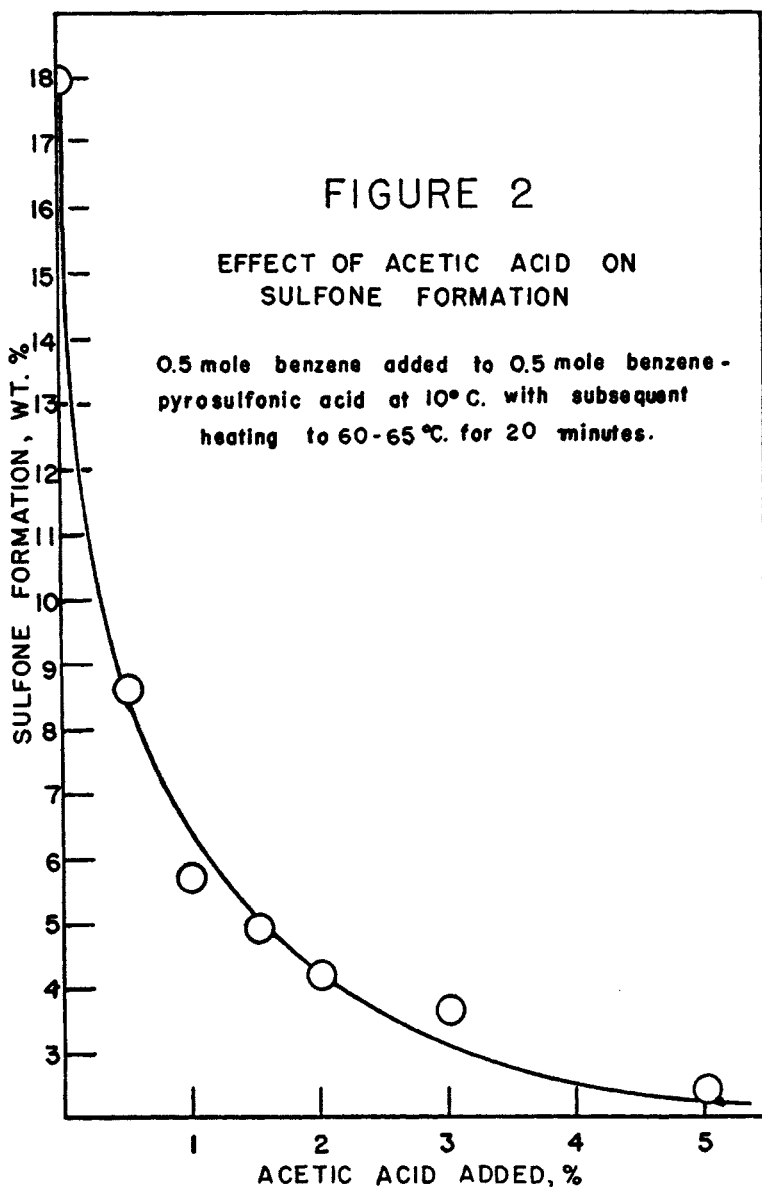
temperature had been reached the temperature fell to 60–65° and was maintained there for 20 minutes. Air was drawn over the product during the last five minutes of the reaction period to assure removal of remaining sulfur dioxide. The results are given in Table II and, graphically, in Figure 2.

TABLE II  
EFFECT OF ACETIC ACID ON SULFONE FORMATION

(0.5 mole of benzene added to 0.5 mole of benzene pyrosulfonic acid at 10° with subsequent heating at 60–65° for 20 minutes)

Acetic Acid Added, weight-%	Sulfone in Product, weight-%
0.	18.10
0.5	8.68
1.0	5.75
1.5	4.92
2.0	4.20
3.0	3.64
5.0	2.48

<sup>a</sup> Based on the combined weight of sulfur trioxide and hydrocarbon used.



The maximum temperatures reached after the second benzene addition, as shown in Table III, were consistently lower when acetic acid was present indicating a combination of the sulfur trioxide with acetic acid and a correspondingly lower energy release upon reaction with benzene.

It was, furthermore, of both theoretical and practical interest to utilize mole ratios of benzene to sulfur trioxide less than 1 in the first step of the process and adding the correspondingly smaller, remaining amount of benzene to finally yield a one to one  $\text{SO}_3\text{-C}_6\text{H}_6$  ratio at 10°. Accordingly, from 50 to 90% of the benzene required for sulfonic acid formation was added to the sulfur trioxide-

sulfur dioxide mixture at  $-9^{\circ}$ . The temperature of this product was subsequently raised to  $10^{\circ}$  with simultaneous expulsion of nearly all of the sulfur dioxide. The remaining benzene required to make benzenesulfonic acid in a 1 to 1 mole ratio of  $\text{SO}_3$  to benzene, was added rapidly at  $10^{\circ}$  whereupon the temperature rose spontaneously to 30 to  $90^{\circ}$ , depending upon the amount of benzene already used in the first step. All products were heated at  $65^{\circ}$  for 20 minutes, with air sweeping over the reaction product during the last five minutes before analysis. As shown in Table III, and in Figure 3, the amount of sulfone formed is dependent upon the amount of benzene added in the first step which in turn is a measure of the pyrosulfonic acid concentration present. The pronounced effect shown by the presence of 1% acetic acid in the sulfonation mixture is also shown in Table III and Figure 3.

It is interesting to note that the  $x$  moles of benzene added in the second step is proportional to the pyrosulfonic acid present in the first step reaction product. Hence, extrapolation of Curve B in Figure 3 indicates that no sulfone should be formed when no pyrosulfonic acid is present.

All the foregoing experiments were performed utilizing a commercial, nitration-

TABLE III  
COMPOSITION OF SULFONATED BENZENE AT VARIOUS MOLE RATIOS OF  
BENZENE TO  $\text{SO}_3$  IN FIRST STEP

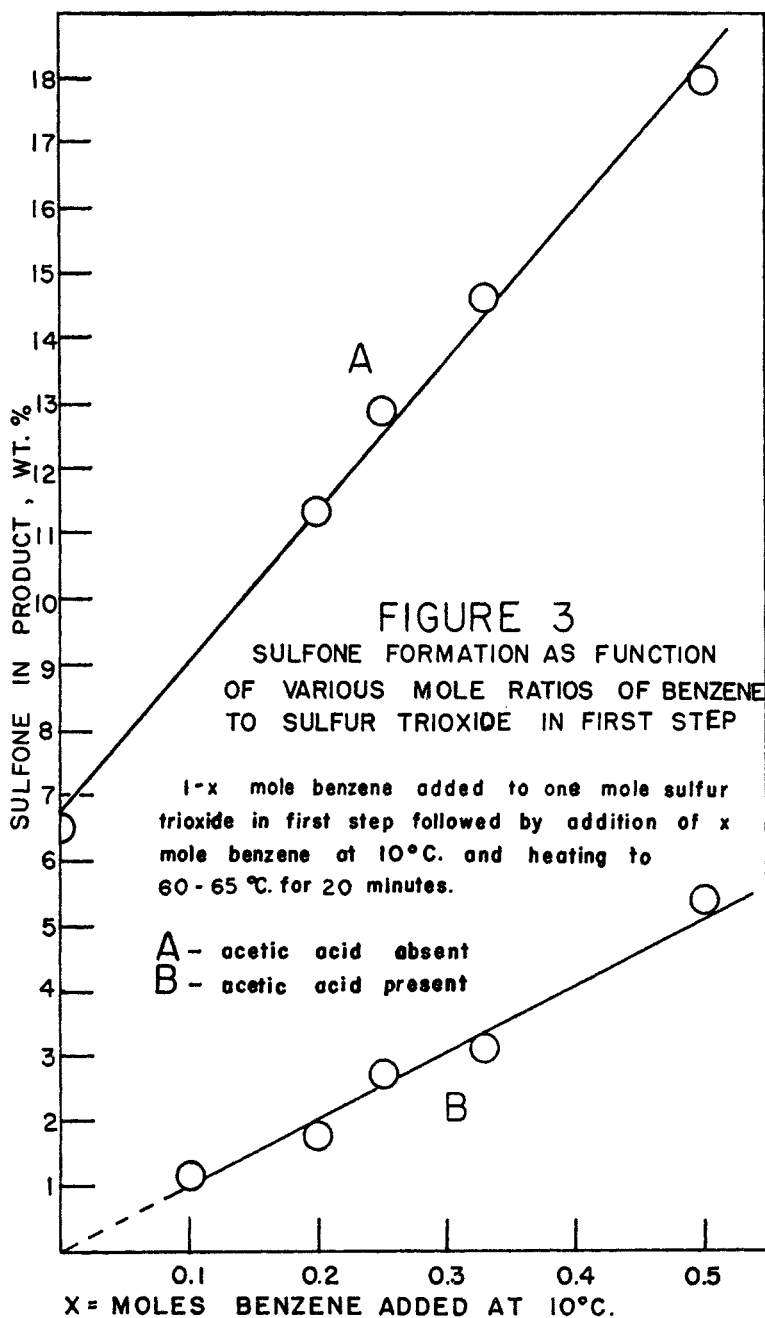
C <sub>6</sub> H <sub>6</sub> Added to 1 mole SO <sub>3</sub> in First Step at $-9^{\circ}$ 1 - x moles	C <sub>6</sub> H <sub>6</sub> Added at $10^{\circ}$ (Moles Pyrosulfonic Acid Present) x moles	Max. Temp. Reached after Addition of x moles Benzene $^{\circ}\text{C}$ .	Analyses of Products			
			Sulfone, weight-%	SO <sub>2</sub> as H <sub>2</sub> SO <sub>4</sub> weight-%	Benzene sulfonic acid, weight-%	Neutralization equivalent, milli-equivalents per gram
<i>A. In the absence of acetic acid</i>						
0.50	0.50	95	18.0	10.1	72.0	6.83
0.67	0.33	68	14.7	9.0	77.0	6.71
0.75	0.25	60	13.0	7.9	79.4	6.63
0.80	0.0	30	11.4	6.3	82.0	6.45
1.00 <sup>a</sup>	0	-9	6.5	6.0	87.3	6.74
<i>B. In the presence of 1% acetic acid<sup>b</sup></i>						
0.50	0.50	90	5.5	6.3	86.6	6.95
0.67	0.33	60	3.2	6.8	88.8	—
0.75	0.25	38	2.8	5.6	90.3	7.03
0.80	0.20 <sup>c</sup>	45 <sup>c</sup>	1.8	2.0	94.4	6.55
0.90 <sup>a</sup>	0.10	-5	1.2	1.6	95.2	6.52

<sup>a</sup> Complete solidification of the product resulted at  $-4$  to  $-6.5^{\circ}$ ; therefore, the entire reaction product was heated to  $50^{\circ}$  to obtain homogeneous reaction conditions.

<sup>b</sup> The acetic acid remains in the product; hence, the total material balance of sulfur containing products is 99%, maximum.

<sup>c</sup> Benzene added to first-stage reaction product at  $20^{\circ}$  instead of  $10^{\circ}$ . Hence, the maximum temperature reached is about  $10^{\circ}$  higher than if the second benzene addition had been made at  $10^{\circ}$ .

All products were heated at  $60$ - $65^{\circ}$  for 20 minutes.



grade of benzene. When pure benzene was used, essentially identical results were obtained. To test the effect of the presence of sulfur compounds in the benzene, 0.5% of thiophene was intentionally added to nitration-grade benzene with no noticeable effect on the composition of the product.

Also, using reagent-grade benzene did not significantly alter the degree of sulfone formation. Thus, utilizing the 75-25 ratio of addition under conditions identical with those given in Table III, there was formed 12.4% diphenylsulfone with reagent-grade benzene in the absence of acetic acid and 2.6% in the presence of 1% acetic acid. These results agree well with those obtained for nitration-grade benzene, 13.0% and 2.8%, respectively.

In separate experiments, the presence of acetic acid in the sulfonation mixture also showed conclusively a lowering of sulfone formation when toluene, xylenes, and ethylbenzene were used as the hydrocarbon. These results are given in Table IV.

Also, various other mono- and di-carboxylic acids exhibit results similar to those obtained with acetic acid. Results obtained with different carboxylic acids in the sulfonation of toluene are given in Table V.

So far as the order of addition is concerned, in the case of benzene, it is pre-

TABLE IV

EFFECT OF 1% GLACIAL ACETIC ACID ON SULFONE FORMATION IN THE  $\text{SO}_2$  SULFONATION OF VARIOUS AROMATIC HYDROCARBONS

(Single stage sulfonation in  $\text{SO}_2$  at  $-9^\circ$  followed by heating the reaction mixture at  $65^\circ$  for 20 minutes)

Hydrocarbon	Mode of Addition	Sulfone in Product, weight-%	
		In presence of acetic acid	In absence of acetic acid
Benzene.....	1	0.8-1.1	5-7
Toluene.....	2	0.1-0.7	1.9-2.5
Ethylbenzene.....	2	0.4-0.5	1.9-2.2
Xylene (mixed).....	3	1.1-1.6	5-6

<sup>a</sup> 1 = Hydrocarbon into  $\text{SO}_2\text{-SO}_3$ .

2 = Simultaneous addition of  $\text{SO}_2\text{-SO}_3$  and hydrocarbon- $\text{SO}_2$  from separate feed vessels into reaction flask.

3 =  $\text{SO}_2\text{-SO}_3$  into hydrocarbon in  $\text{SO}_2$ .

TABLE V

EFFECT OF 1% OF VARIOUS CARBOXYLIC ACIDS ON THE FORMATION OF DITOLYL SULFONE<sup>a</sup>

Carboxylic Acid	Composition of Products		
	$\text{SO}_2$ as $\text{H}_2\text{SO}_4$ , weight-%	Ditolyl sulfone in product, weight-%	Toluene sulfonic acid, weight-%
None.....	—	2.0	96.1
Acetic.....	1.86	0.37	96.5
Malonic.....	2.06	0.84	95.8
Azelaic.....	1.65	0.60	96.7
Benzoic.....	1.96	0.62	96.0

<sup>a</sup> Toluene, containing 1% of the carboxylic acid, based on the total reaction mass, and  $\text{SO}_2$  in  $\text{SO}_2$  were added to a reaction vessel from two separate reservoirs at approximately equivalent rates maintaining a 1 to 1  $\text{SO}_2$  to hydrocarbon ratio followed by heating the reaction mixture at  $65^\circ$  for 20 minutes. See experimental section for other details.



ferred to add the hydrocarbon to the  $\text{SO}_2$ - $\text{SO}_3$  mixture rather than to reverse the procedure. In one set of experiments, as is evident from Figure 3, curve B, the amount of diphenyl sulfone found in the presence of 1% acetic acid is 0.5% or less, whereas, under identical conditions, the reverse procedure yields sulfone in excess of 1%. This fact was also recognized by Leierson, Bost, and LeBaron (5), and is to be expected from mass action effects.

#### EXPERIMENTAL

*Materials.* Benzene, Pure, Merck and Company and J. T. Baker Company. Benzene, Reagent-grade, Merck and Company. Benzene, Nitration-grade, Tennessee Coal and Iron Company. Ethylbenzene, Dow Chemical Company. Xylene, Merck and Company. Acetic Acid, Glacial, Reagent Grade, E. I. du Pont de Nemours and Company. Sulfur Dioxide, Highest Quality, Tennessee Corporation. Sulfur Trioxide, freshly distilled from Tennessee Corporation's 20% oleum. Thiophene, Socony-Vacuum Oil Company, Inc.

*Procedure. Sulfonation of benzene.* Into a 1-liter, 3-neck flask, equipped with a mechanical stirrer, thermometer, dropping-funnel, and vent tube ending in a  $\text{CaCl}_2$  trap, there was placed 500 ml. of liquid  $\text{SO}_2$  and 1.00 to 1.05 gram-moles of sulfur trioxide. One gram-mole of benzene was added from the funnel whose stem was sufficiently long to reach below the  $\text{SO}_2$  surface in the flask. The actual amounts of reagents used may be varied within wide limits maintaining, however, the indicated mole ratios of reagents and solvent. Either all of the benzene is added dropwise at  $-9^\circ$  or in two portions adding  $1 - x$  mole at  $-9^\circ$  followed by heating the reaction mixture to  $10^\circ$  and adding the remaining  $x$  mole of benzene. In those cases where acetic acid was used, it was added to the  $\text{SO}_2$ - $\text{SO}_3$  mixture. Prevailing conditions for a typical run using 89.64 g. of  $\text{SO}_3$ , 1.8 g. of glacial acetic acid, and 87.5 g. of benzene (mole ratio benzene to  $\text{SO}_3$ , 1 to 1) were as follows:

Time (minutes)	T, $^\circ\text{C}$ .	Remarks
0	-9	65.6 g. of benzene started in
12	-9	first stage benzene addition completed
45	-5	thin clear liquid
51	0	thin clear liquid
56	+5	thin clear liquid
57	+6	thin slush forming
61	+10	2nd addition, 21.9 g. of benzene made quickly
62	+39	addition completed, temperature rose to $39^\circ$ , heat applied
64	+60	thin clear liquid
79	+61	air sweeping over product started to remove residual $\text{SO}_2$
83	+63	run weighed
Weight of product	173.8 g.	
Weight put into run	178.94 g.	
Weight lost through exhaust	5.14 g. ( $\text{SO}_3$ and benzene)	
% weight lost through exhaust	2.87%	
Melting point of acid	$60^\circ$ (the pure anhydrous acid melts at $66^\circ$ )	
Color	pink to tan	
Residual $\text{SO}_2$	less than 0.01%	
Sulfone	2.18%	
$\text{H}_2\text{SO}_4$	1.52%	
Neutralization equivalent	6.47 m.e./g.	
AcOH	1.00%	
Benzenesulfonic acid	94.60%	
Conversion based on benzene	96.3% (average conversion 96-97%)	
$\text{H}_2\text{O}$ (difference)	0.70%	

*Sulfonation of other hydrocarbons.* Toluene, xylene, ethylbenzene and, in a few instances, benzene were sulfonated, in the same type apparatus as described above, by adding the SO<sub>2</sub> solution of SO<sub>2</sub> to an SO<sub>2</sub> solution of the hydrocarbon. In a few experiments, utilizing toluene and ethylbenzene the SO<sub>2</sub>-SO<sub>2</sub> mixture and the hydrocarbon in SO<sub>2</sub> were allowed to run from two separate feed vessels into liquid SO<sub>2</sub> in an approximate 1 to 1 SO<sub>2</sub>-hydrocarbon molar ratio, to avoid an excess of either reagent at any one instance.

Contrary to the findings experienced with benzene, alkylbenzenes and, especially, toluene and ethylbenzene were sulfonated best by either the simultaneous addition method or by the addition of SO<sub>2</sub> to the hydrocarbon. This preference is based on the suspicion that alkylbenzenes tend to form disulfonated derivatives more readily than benzene.

Carboxylic acids, when used, were added to the liquid SO<sub>2</sub> in the reaction flask for simultaneous addition runs. For runs in which SO<sub>2</sub>-SO<sub>2</sub> was added to the hydrocarbon, the carboxylic acid was first added to the hydrocarbon.

The following is a typical example in which 100.5 g. of SO<sub>2</sub>, dissolved in 450 ml. of liquid SO<sub>2</sub>, was added to the reaction flask simultaneously from a separate vessel, with 110.0 g. of toluene in 150 ml. of liquid SO<sub>2</sub> containing 2.0 g. of glacial acetic acid. The toluene was added below the SO<sub>2</sub> surface in the reaction flask.

Time (minutes)	Temperature, °C.	Remarks
0	-10	Addition started
12½	-9	Addition finished
37	+10	
62	+50	Air sweeping started
77	+50	Run finished

Weight of finished product.....	210.5 g.
Weight put into run.....	212.54 g.
Weight lost through exhaust.....	2.04 g. = 0.86% of total
Average conversion to toluenesulfonic acid.....	96-97%

In both methods, the amount of residual SO<sub>2</sub>, after air sweeping at 50-65° was less than 0.01%.

*Analyses. Neutralization equivalent.* Approximately 5 g. of the molten and well mixed sulfonic acid is weighed (±0.001 g.) into a 250-ml. volumetric flask. A small vial equipped with a stopper and a medicine dropper is recommended for this weighing. Exposure of the vial contents to the air are kept to the minimum to prevent moisture from being absorbed by the anhydrous acid.

The sample is diluted to 250 ml. with distilled water and the flask is inverted 50 times or more to insure thorough mixing. Two 25-ml. aliquots are pipetted into 400-ml. beakers and titrated with 0.1 N NaOH solution to a permanent pink color of phenolphthalein indicator.

$$\text{Neutralization equivalent} = \frac{\text{ml. NaOH} \times N \text{ NaOH}}{\text{wt. of sample g}/10} = \text{m.e./gram.}$$

Because of the use of carboxylic acids in some experiments, a correction factor in the m.e./g., as determined above, must be applied. The milli-equivalence of acetic acid per gram of sample when 1% of glacial acetic acid, based on benzenesulfonic acid, is used amounts to 0.167 and this value must be subtracted from the total m.e. determined above. The corrected result is to be used in the sulfonic acid determination.

*Sulfone determination.* A 50-g. sample of molten, well mixed sulfonic acid is weighed out in a 600-ml. beaker (±0.1 g.). The sample is dissolved in 250 ml. of distilled water and neutralized to just a permanent pink color of phenolphthalein with 25% NaOH solution. After cooling to 15-20° in the refrigerator, this solution is extracted with 100 ml. of diethyl ether by shaking thoroughly in a 1-liter separatory-funnel. The ether layer is transferred to a 500-ml. separatory-funnel. The aqueous solution then is extracted twice again with two 50-ml. portions of ether. When the amount of sulfone exceeds 6%, up to 600 ml. of ethyl ether are required for extraction. The combined ether extracts then are washed by

shaking with 50 ml. of cool water. The total aqueous solution, including the wash water, is warmed to remove ether and saved for the sulfuric acid analysis.

The ether containing the sulfone is evaporated from a tared 250-ml. Erlenmeyer flask in a hot water bath (hood).

After all the ether has been boiled off, the flask is placed in an oven at 120° until constant weight is reached (to 0.01 g.). After cooling in a desiccator the flask is weighed ( $\pm 0.01$  g.).

$$\% \text{ Sulfone} = \frac{\text{weight sulfone g.} \times 100}{50}$$

*Sulfuric acid determinations.* The aqueous solution from the sulfone determination, after all the ether has been boiled out, is transferred to a 500-ml. volumetric flask and brought to volume with washings from the beaker. After thoroughly mixing the contents of the flask, two 50-ml. aliquots are pipetted into 600-ml. beakers. These samples are acidified with 1 ml. of concentrated HCl and then are diluted to 350 ml. with distilled water and placed on the hot plate.

When the temperature nears the boiling point, 20 ml. of 10% BaCl<sub>2</sub> solution is added to each sample to precipitate BaSO<sub>4</sub>. After digesting the samples for 45 minutes just below the boiling point, the BaSO<sub>4</sub> is filtered through a double No. 40 Whatman 12.5 cm. fluted filter paper. The beaker and precipitate are then washed 12 times with a small stream of hot water from a wash bottle.

The samples are ignited in crucibles at 700° in a muffle furnace with the door cracked open to prevent reduction of the BaSO<sub>4</sub>. The BaSO<sub>4</sub> is weighed and the per cent H<sub>2</sub>SO<sub>4</sub> is calculated as follows:

$$\% \text{ H}_2\text{SO}_4 = \frac{\text{weight BaSO}_4 \text{ g.} \times 0.42 \times 100}{5}$$

*Total sulfonic acid.* Neutralization equivalent

$$\text{m.e./g.} - \text{H}_2\text{SO}_4 \text{ m.e./g.} \times \frac{\text{mol. wt. of Sulfonic Acid}}{10} = \% \text{ Sulfonic Acid.}$$

In those cases where carboxylic acids were used, proper correction factors, as shown above, must first be applied to the neutralization equivalent.

#### SUMMARY

The sulfur trioxide sulfonation of simple aromatic hydrocarbons produces sulfonic acids in high yield along with lesser amounts of sulfones. The amount of sulfone formed depends upon the temperature of reaction, the mode of addition of the reagents and, especially, upon the presence of small amounts of carboxylic acids, intentionally added to the reaction mixture.

These factors lead to the conclusion that pyrosulfonic acids are probably precursors to sulfones in the sulfonation of aromatic hydrocarbons with sulfur trioxide.

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