

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

THE SULFONATION OF SOME AROMATIC COMPOUNDS
USING SULFURIC ACID
IN THE PRESENCE OF THIONYL CHLORIDE

BY

PAUL JUERGENS

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1955

625-1-18

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1955

Abstract

The rate of reaction in the sulfonation of some aromatic compounds with sulfuric acid was increased by the presence of thionyl chloride which, by reacting with the water of formation, effectively maintained the concentration of sulfuric acid above the level at which sulfonation can occur. The thionyl chloride had no measurable effect on the formation of isomers.

The sulfonation reactions studied included those of toluene, naphthalene, bromobenzene, ortho-bromotoluene, and chlorobenzene.

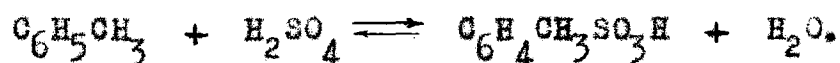
TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURE	3
III. ANALYTICAL PROCEDURE	4
IV. EXPERIMENTAL RESULTS AND DATA	6
Sulfonation of Toluene	6
Sulfonation of Naphthalene	11
Sulfonation of Bromobenzene	16
Sulfonation of Ortho-Bromotoluene	18
Sulfonation of Chlorobenzene	20
V. SUMMARY	22
VI. CONCLUSIONS	23
VII. MELTING POINT CURVE	30
VIII. LITERATURE CITED	31

I. INTRODUCTION

The sulfonation of aromatic compounds has been accomplished by the use of a number of sulfonating agents, among which are included fluorosulfonic acid, chlorosulfonic acid, salts of chlorosulfonic acid, chlorosulfonic anhydride, sulfamic acid, oleum, and sulfuric acid in varying concentrations and in the presence of various catalysts. Among some of the substances which have been used as catalysts in sulfonations are iodine⁽¹⁾, mercury and its salts, vanadium and its salts, and boric acid.

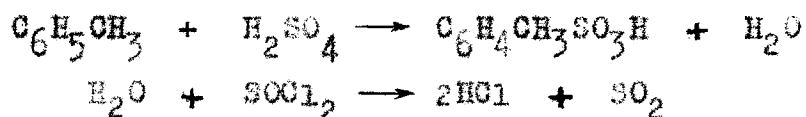
When sulfuric acid is used in sulfonations, the reaction stops if the sulfuric acid concentration is reduced to a certain point which varies with the temperature, and differs with each compound treated. This limiting concentration is defined as the π value⁽²⁾. In the sulfonation of toluene, water is formed as a product,



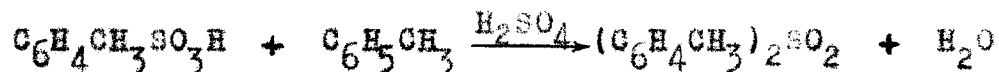
In order to maintain the concentration of sulfuric acid sufficiently high for sulfonation to proceed, the water formed in the reaction must be removed. This can be done by either physical or chemical methods. The physical removal of water has been accomplished by such methods as

passing the aromatic vapor through hot sulfuric acid, by distilling the water under reduced pressure, or by using an inert gas. Sulfonation has also been reported facilitated by the use of boron fluoride⁽³⁾ or hydrogen fluoride⁽⁴⁾, which reacted with the water of formation to maintain the concentration of the sulfuric acid above the lower limit at which sulfonation can occur.

The study of the effect on the equilibrium of some sulfonation reactions using thionyl chloride to remove the water of formation is reported in this paper. The removal of the water is indicated by the equations:



The formation of sulfone occurs as a side reaction according to the equation:



The water formed in this reaction must also be removed by the thionyl chloride.

The sulfonation reactions reported are those of toluene, naphthalene, bromobenzene, ortho-bromotoluene, and chlorobenzene. Agitation was not used in reactions carried out at reflux temperature.

II. EXPERIMENTAL PROCEDURE

The actual conditions of sulfonation are reported with each experimental sulfonation. However, the following general procedure was used in preparing the samples for analysis, with certain exceptions noted:

A. The excess volatile matter was removed by aspiration. The temperature and length of time of aspiration were reported with each sulfonation.

B. The sulfonation mixture was diluted with cold water and the remaining volatile solvent was driven off by heating the aqueous solution. In the sulfonation of naphthalene, excess naphthalene was removed by filtration and the aqueous solution was then heated to drive off volatile materials.

C. After the aqueous solution had been allowed to cool, it was filtered into a volumetric flask and the water-insoluble matter was filtered out, dried, and weighed. The filtrate in the volumetric flask was diluted to the mark with distilled water and analysed. In the sulfonation of naphthalene, excess naphthalene was removed together with any sulfones which may have formed.

III. ANALYTICAL PROCEDURES

A. Determination of Sulfonic Acid

Total acidity of the reaction mix was found by titrating an aliquot portion of the water solution to the phenolphthalein end point with a standard solution of sodium hydroxide. Corrections were made for hydrochloric acid and sulfuric acid present and the result was reported as sulfonic acid.

B. Determination of Chlorides

The correction for chlorides was made by neutralizing an aliquot portion of the water solution with calcium carbonate and titrating with a standard solution of silver nitrate. Potassium chromate was used as the indicator.

C. Determination of Unreacted Sulfuric Acid

An aliquot portion of the water solution was taken, diluted to 200 ml. with distilled water and brought to a boil after adding 5 ml. of 6 N hydrochloric acid. The sulfate was precipitated with a 25 per cent solution of barium chloride and allowed to digest. The precipitate was filtered, ignited, and then weighed as barium sulfate.

D. Preparation of the Sulfonamide Derivative⁽⁵⁾

A five gram sample of the dried sodium salt of the sulfonic acid was reacted with 12.5 grams of PCl_5 to form

the sulfonyl chloride. The amide was prepared from the sulfonyl chloride by mixing with concentrated ammonia.

The sulfonamide was prepared to determine the isomers of sulfonic acid present at the end of the sulfonation reaction, since the melting point of the sulfonic acid is usually too low for this determination. The percentage of each isomer present may be determined from the melting point curve of the sulfonamides of the isomers. If two compositions on the curve are possible for the observed melting point of an experimental sample, one of the possible compositions may be eliminated by adding a pure sample of one of the isomers to the experimental sample. The melting point of the mixed sample thus obtained will then be either higher or lower than that of the original experimental sample and will show which of the two possible compositions was correct for the original experimental sample.

IV. EXPERIMENTAL RESULTS AND DATA

A. Sulfonation of Toluene

Experimental Run 1

Mole ratios. 2.82 moles toluene : 1 mole sulfuric acid : 1.12 moles thionyl chloride.

Reaction conditions. To a 500 ml. round-bottom flask were added 13.9 gm. toluene, 5.25 gm. sulfuric acid, and 7.14 gm. thionyl chloride. The flask was attached to a water-cooled condenser, and the contents were agitated with a magnetic pole stirring bar and motor at room temperature for one hour (the mixture was homogeneous after 50 minutes). The flask was then stoppered and allowed to stand four days at room temperature, at the end of which time the excess volatile matter was removed by aspirating 45 minutes, with heat applied during the last 15 minutes of aspiration.

Some of the reaction mixture was lost during aspiration. For this reason, the yield reported for sulfonic acid on this run is rejected.

Results. Reacted Sulfuric Acid (sulfonic acid). (Rejected--71.0%)
 Unreacted Sulfuric Acid. Nil
 Water Insoluble Matter Nil

Experimental Run 2

Mole ratios. 3 moles toluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 41.4 gm. toluene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled condenser was attached and the mixture was agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for one hour. The mixture was then aspirated 15 minutes, stoppered, and allowed to stand at room temperature for four days, after which the excess toluene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 97.1%
 Unreacted Sulfuric Acid. Nil
 Water Insoluble Matter (sulfone) Nil

Experimental Run 3

Mole ratios. 3 moles toluene : 1 mole sulfuric acid.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 41.4 gm. toluene and 14.7 gm. sulfuric acid. A water-cooled condenser was attached and the mixture was agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for a period

of three and one-half hours. The mixture was then aspirated five minutes at room temperature and the excess toluene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 31.9%
 Unreacted Sulfuric Acid. 66.5%
 Water Insoluble Matter (sulfone) Nil

Experimental Run 4

Mole ratios. 3 moles toluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 41.4 gm. toluene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled reflux condenser was attached and the mixture was agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for a period of two hours. The mixture was then aspirated for 20 minutes and the excess toluene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 88.4%
 Unreacted Sulfuric Acid. 7.5%
 Water Insoluble Matter (sulfone) Nil
 Melting Point of Sulfonamide Derivative. . . 130°C.

Experimental Run 18

Mole ratios. 3 moles toluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 27.6 gm. toluene, 9.8 gm. sulfuric acid, and 14.3 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the reflux condenser, and the mixture was allowed to reflux for one hour. The mixture was then aspirated for 15 minutes at room temperature and excess toluene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 52.5%
 Unreacted Sulfuric Acid. 40.7%
 Water Insoluble Matter (sulfone) 0.8%

Experimental Run 19

Mole ratios. 3 moles toluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 41.4 gm. toluene, 14.7 gm. sulfuric acid, and 21.2 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the reflux condenser, and the mixture was allowed to reflux for

one hour. The volatile matter was then removed by aspirating for 30 minutes at room temperature and the excess toluene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid). 54.1%
 Unreacted Sulfuric Acid. 26.8%
 Water Insoluble Matter (sulfone) 0.3%
 Melting Point of Sulfonamide Derivative. . 137.5°C.

Experimental Run 22

Mole ratios. 3 moles toluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 250 ml. Erlenmeyer flask were added 41.4 gm. toluene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled condenser was attached, and the mixture was agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for fifteen minutes. The mixture was then aspirated with agitation at room temperature for 30 minutes, and the excess toluene was steam distilled. Less than 0.5 per cent of the original thionyl chloride was present in the mixture after the aspiration and distillation.

Results. Reacted Sulfuric Acid (sulfonic acid). 88.2%

Unreacted Sulfuric Acid. 6.9%
 Water Insoluble Matter (sulfone) Nil

B. Sulfonation of Naphthalene

Experimental Run 5

Mole ratios. 2 moles naphthalene : 1 mole
 sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom
 ground-glass flask were added 38.45 gm. naphthalene,
 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride.
 A water-cooled reflux condenser was attached, a
 thermometer was lowered into the flask through the
 reflux condenser, and the mixture was allowed to
 reflux for one hour. At the end of the reaction the
 product mixture was viscous and deep black in color.
 The excess naphthalene was removed by filtering.

Results. Reacted Sulfuric Acid (sulfonic
 acid). 58.6%
 Unreacted Sulfuric Acid. 15.8%
 Melting Point of Sulfonamide Derivative. . 209.5°C.

Experimental Run 10

Mole ratios. 1 mole naphthalene : 1 mole
 sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 19.2 gm. naphthalene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the reflux condenser, and the mixture was allowed to reflux for 20 minutes. The product mixture was deep black in color at the end of the reaction, but less viscous than that of Run 5. Excess naphthalene was removed by filtering.

Results. Reacted Sulfuric Acid (sulfonic acid). 43.5%
Unreacted Sulfuric Acid. 24.5%

Experimental Run 12

Mole ratios. 1.2 moles naphthalene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 23.1 gm. naphthalene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled condenser was attached and the mixture was agitated with a glass-covered magnetic pole stirring bar and motor at room temperature for two hours. The mixture began taking on a black color immediately after agitation was started, and the reaction flask

was about half filled with foam 20 minutes after agitation was started. The product mixture was black and viscous at the end of the run. The excess naphthalene was removed by filtering.

Results. Reacted Sulfuric Acid (sulfonic acid). 42.1%
Unreacted Sulfuric Acid. 39.7%

Experimental Run 13

Mole ratios. 1.2 moles naphthalene : 1 mole sulfuric acid : 1.2 moles thionyl chloride : 1.2 moles chloroform.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 23.1 gm. naphthalene, 21.4 gm. thionyl chloride, and 21.5 gm. chloroform. Agitation was begun with a magnetic pole stirring bar and motor, and 14.45 gm. sulfuric acid were added in three portions over a period of 20 minutes. Agitation at room temperature was then continued for 15 minutes more. At the end of this period, the mixture was diluted with water, heated to drive off the chloroform, and the excess naphthalene was removed by filtering.

Foaming was noted after each addition of sulfuric acid. The reaction mixture was black at the end of the run.

Results. Reacted Sulfuric Acid (sulfonic acid). 63.1%
 Unreacted Sulfuric Acid. 24.7%

Experimental Run 14

Mole ratios. 1.2 moles naphthalene : 1 mole sulfuric acid : 1.2 moles thionyl chloride : 1.2 moles chloroform.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 23.1 gm. naphthalene, 21.4 gm. thionyl chloride, and 21.5 gm. chloroform. A water-cooled condenser was attached, agitation at room temperature was begun with a magnetic pole stirring bar and motor, and 14.9 gm. sulfuric acid were added in four portions (4.8, 3.3, 3.9, and 2.9 gm.), each at an interval of 20 minutes. Agitation was then continued an additional three and one-fourth hours. The chloroform was then removed by heating the mixture and the excess naphthalene was removed by filtering.

The reaction mixture was black in color within five minutes after addition of the first portion of sulfuric acid, and foaming was noted after addition of each portion of acid.

Results. Reacted Sulfuric Acid (sulfonic acid). 82.2%

Unreacted Sulfuric Acid. 11.6%
Melting Point of Sulfonamide Derivative. . . 138°C.

Experimental Run 17

Mole ratios. 1.2 moles naphthalene : 1 mole
sulfuric acid : 1.2 moles thionyl chloride : 1.2 moles
chloroform.

Reaction conditions. To a 500 ml. Erlenmeyer
flask were added 23.1 gm. naphthalene, 14.7 gm. sulfuric
acid, 21.4 gm. thionyl chloride, and 21.5 gm. chloro-
form (the liquids were chilled to approximately 10°C.
before adding them to the flask). The flask was
partially submerged in a water bath through which cold
tap water at 6.5°C. to 7.0°C. was continuously cir-
culated, a water-cooled condenser was attached to the
flask, and the mixture was agitated with a glass-
covered magnetic pole stirring bar and motor for a
period of four and one-half hours. The temperature of
the mixture, which was checked frequently with a
thermometer lowered through the condenser, varied from
8°C. to 11°C., with an average of about 9°C. At the
end of the run, the mixture was diluted with cold
distilled water, the excess naphthalene was filtered
out, and the chloroform was removed by heating the
mixture.

Results. Reacted Sulfuric Acid (sulfonic acid). 63.0%
 Unreacted Sulfuric Acid. 29.3%
 Melting Point of Sulfonamide Derivative. . . 143°C.

C. Sulfonation of Bromobenzene

Experimental Run 6

Mole ratios. 3 moles bromobenzene : 1 mole sulfuric acid : 1 mole thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 47.1 gm. bromobenzene, 9.8 gm. sulfuric acid, and 11.9 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the condenser, and the mixture was allowed to reflux for two and one-half hours. The mixture was homogeneous after two hours. The excess bromobenzene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid). 75.4%
 Unreacted Sulfuric Acid. 18.9%
 Water Insoluble Matter (sulfone) 1.3%

Experimental Run 7

Mole ratios. 3 moles bromobenzene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. Same as Experimental Run 6, except that the reflux time was reduced to one-half hour. The mixture was homogeneous and gas evolution had stopped after refluxing for 20 minutes.

Results. Reacted Sulfuric Acid (sulfonic acid). 77.2%
 Unreacted Sulfuric Acid. 22.9%
 Water Insoluble Matter (sulfone) 0.7%

Experimental Run 16

Mole ratios. 3 moles bromobenzene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 70.7 gm. bromobenzene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled condenser was attached and the mixture was agitated at room temperature with a magnetic pole stirring bar and motor for four and one-half hours. The mixture was not homogeneous at the end of the run. The excess bromobenzene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid). 33.0%
 Unreacted Sulfuric Acid. 63.1%
 Water Insoluble Matter (sulfone) Nil
 Melting Point of Sulfonamide Derivative. . . 165°C.

D. Sulfonation of Ortho-bromotoluene

Experimental Run 8

Mole ratios. 3 moles ortho-bromotoluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 51.3 gm. ortho-bromotoluene, 9.8 gm. sulfuric acid, and 14.3 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the condenser, and the mixture was allowed to reflux for two hours. Some of the reaction mixture was lost when an attempt was made to steam distill the excess ortho-bromotoluene.

Results. Water Insoluble Matter (sulfone) Nil

Experimental Run 9

The same mole ratios and reaction conditions which were used in Experimental Run 8 were also used in this run, except that the reflux time was increased to two and three-fourths hours.

Results. Reacted Sulfuric Acid (sulfonic acid). 53.9%
Unreacted Sulfuric Acid. 22.4%
Water Insoluble Matter (sulfone) Nil

Experimental Run 11

The same mole ratios and reaction conditions which

were used in Experimental Runs 8 and 9 were also used in this run, except that the reflux time was reduced to 45 minutes. The mixture was homogeneous after 40 minutes.

Results. Reacted Sulfuric Acid (sulfonic acid). 43.2%
 Unreacted Sulfuric Acid. 29.1%
 Water Insoluble Matter (sulfone) Nil

Experimental Run 15

Mole ratios. 3 moles ortho-bromotoluene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 500 ml. Erlenmeyer flask were added 77.0 gm. ortho-bromotoluene, 14.7 gm. sulfuric acid, and 21.4 gm. thionyl chloride. A water-cooled condenser was attached and the mixture was agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for two and one-fourth hours. The mixture was then diluted with water and heated to drive off volatile matter and to steam distill the excess ortho-bromotoluene.

Results. Reacted Sulfuric Acid (sulfonic acid). 60.1%
 Unreacted Sulfuric Acid. 37.2%
 Water Insoluble Matter (sulfone) Nil

E. Sulfonation of ChlorobenzeneExperimental Run 20

Mole ratios. 3 moles chlorobenzene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 200 ml. round-bottom ground-glass flask were added 33.8 gm. chlorobenzene, 9.8 gm. sulfuric acid, and 14.3 gm. thionyl chloride. A water-cooled reflux condenser was attached, a thermometer was lowered into the flask through the condenser, and the mixture was allowed to reflux for 15 minutes, after which the mixture was homogeneous. (Gas was evolved throughout the entire run.) The mixture was then aspirated for 30 minutes and the excess chlorobenzene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 69.5%
 Unreacted Sulfuric Acid. 25.3%
 Water Insoluble Matter (sulfone) 0.7%

Experimental Run 21

Mole ratios. 3 moles chlorobenzene : 1 mole sulfuric acid : 1.2 moles thionyl chloride.

Reaction conditions. To a 250 ml. Erlenmeyer flask were added 33.8 gm. chlorobenzene, 9.8 gm. sulfuric acid, and 14.3 gm. thionyl chloride. A water-cooled condenser was attached and the mixture was

agitated at room temperature with a glass-covered magnetic pole stirring bar and motor for four and one-half hours. (The mixture was homogeneous after three hours of agitation. Gas evolution occurred throughout the entire run.) The mixture was then aspirated with agitation for 20 minutes and the excess chlorobenzene was steam distilled.

Results. Reacted Sulfuric Acid (sulfonic acid) 87.2%
Unreacted Sulfuric Acid. 15.8%
Water Insoluble Matter (sulfone) 1.0%
Melting Point of Sulfonamide Derivative. . . . 145°C.

V. SUMMARY

RUN	REACTANTS (MOLES)			YIELD (PER CENT)			CONDITIONS
	Aromatic Compound	Sulfuric Acid	Thionyl Chloride	Sulfonic Acid	Sulfuric Acid	Sulfone	
1. Toluene	2.82	1.00	1.12	(71.0)*	Nil	Nil	Room temp. (25°C.), 1 hr. followed by 4 days without agitation.
2. Toluene	3.00	1.00	1.20	97.1	Nil	Nil	Room temp. (26°C.), 1 hr. followed by 4 days without agitation.
3. Toluene	3.00	1.00	0.00	31.9	66.5	Nil	Room temp. (25°C.), 3 1/2 hrs.
4. Toluene	3.00	1.00	1.20	88.4	7.5	Nil	Room temp. (25°C.), 2 hrs.
18. Toluene	3.00	1.00	1.20	52.5	40.7	0.8	Reflux (80°C.), 1 hr.
19. Toluene	3.00	1.00	1.20	54.1	26.8	0.3	Reflux (100°C.), 1 hr.
22. Toluene	3.00	1.00	1.20	88.2	6.9	Nil	Room temp. (24°C.), 1 hr.
5. Naphthalene	2.00	1.00	1.20	58.6	15.8	-	Reflux (170°C.), 1 hr.
10. Naphthalene	1.00	1.00	1.20	43.5	24.5	-	Reflux (150°C.), 1/3 hr.
12. Naphthalene	1.20	1.00	1.20	42.1	39.7	-	Room temp. (23°C.), 2 hrs.
13. Naphthalene	1.20	1.00	1.20	63.1	24.7	-	Room temp. (24°C.), in chloroform, 1/4 hr.
14. Naphthalene	1.20	1.00	1.20	82.2	11.6	-	Room temp. (21°C.), in chloroform, 3 1/4 hrs.
17. Naphthalene	1.20	1.00	1.20	63.0	29.3	-	Cooled (9°C.), in chloroform, 4 1/2 hrs.
6. Bromobenzene	3.00	1.00	1.00	75.4	18.9	1.3	Reflux (150°C.), 2 1/2 hrs.
7. Bromobenzene	3.00	1.00	1.20	77.2	22.9	0.7	Reflux (150°C.), 1/2 hr.
16. Bromobenzene	3.00	1.00	1.20	33.0	63.1	Nil	Room temp. (19°C.), 4 1/2 hrs.
8. Ortho-bromotoluene	3.00	1.00	1.20	-	-	Nil	Reflux (175°C.), 2 hrs.
9. Ortho-bromotoluene	3.00	1.00	1.20	53.9	22.4	Nil	Reflux (175°C.), 2 3/4 hrs.
11. Ortho-bromotoluene	3.00	1.00	1.20	43.2	29.1	Nil	Reflux (175°C.), 3/4 hr.
15. Ortho-bromotoluene	3.00	1.00	1.20	60.1	37.2	Nil	Room temp. (24°C.), 2 1/4 hrs.
20. Chlorobenzene	3.00	1.00	1.20	69.5	25.3	0.7	Reflux (100°C.), 1/4 hr.
21. Chlorobenzene	3.00	1.00	1.20	87.2	15.8	1.0	Room temp. (24°C.), 4 1/2 hrs.

*Rejected

VI. CONCLUSIONS

A. Sulfonation of Toluene

The presence of thionyl chloride promoted the sulfonation of toluene when used in slight molar excess with respect to sulfuric acid. When a ratio of three moles of toluene to one mole of sulfuric acid was used in the presence of thionyl chloride at room temperature, 88.2 per cent of the sulfuric acid reacted to form toluenesulfonic acid after one hour of agitation. After 2.3 hours of agitation at room temperature, the yield of sulfonic acid was 88.4 per cent, and when one hour of agitation at room temperature was followed by four days of standing at room temperature without agitation, the yield of sulfonic acid was 97.1 per cent. The yield after one hour at reflux temperature without agitation was 54.1 per cent. When thionyl chloride was omitted, the yield of sulfonic acid following three and one-half hours of agitation at room temperature was 31.9 per cent. Little or no sulfone formation was observed in the toluene sulfonation reactions.

The thionyl chloride had no measurable influence upon the formation of isomers. This was shown by sulfonamide melting point determinations using the

product mixtures from two sulfonation reactions, one reaction carried out at room temperature and the other at reflux temperature. The melting point of the sulfonamide prepared from the product of the room temperature reaction was 130°C ., indicating the presence of isomers. A mixed melting point determined by adding para-toluenesulfonamide indicated that the composition of the experimental sample was on the para-toluenesulfonamide side of the eutectic point on the melting point curve⁽⁷⁾ and showed that the mixture was 87 per cent para-toluenesulfonamide. The product from the sulfonation reaction carried out at reflux temperature yielded a sulfonamide with a melting point of 137.5°C ., which similarly indicated the presence of 100 per cent para-toluenesulfonamide. Since the para isomer is normally formed in larger amounts at higher temperatures, it is concluded that the presence of the thionyl chloride had no measurable influence upon the formation of isomers.

Harkins⁽⁹⁾ reported the reaction of 87.5 per cent of the sulfuric acid to form sulfonic acid after four hours of agitation at room temperature when a similar ratio of three moles of toluene to one mole of sulfuric acid was used in the presence of thionyl chloride.

After one-half hour of agitation at room temperature followed by three hours at 70°C., 94.0 per cent of the sulfuric acid reacted to form sulfonic acid, of which 95 per cent was the para isomer. These results are in general agreement with those of this report. Harkins' use of agitation is responsible for the differences in the results reported for the reactions at reflux temperature.

B. Sulfonation of Naphthalene

When a ratio of 1.2 moles of naphthalene to one mole of sulfuric acid was used at room temperature in the presence of thionyl chloride, 42.1 per cent of the sulfuric acid reacted to form naphthalenesulfonic acid after two hours of agitation. The presence of the thionyl chloride resulted in charring of the naphthalene to some extent. The charring was reduced and the rate of reaction was increased when chloroform was added in molar quantities equal to that of naphthalene in the mixture. When chloroform was added, 63.1 per cent of the sulfuric acid reacted to form naphthalenesulfonic acid after 15 minutes of agitation at room temperature. In the presence of chloroform, the yield of naphthalenesulfonic acid was increased to 82.2 per cent when the time was increased to three and one-fourth hours, and when the temperature was reduced to

9°C., and the time increased to four and one-half hours, the yield of naphthalenesulfonic acid decreased to 63.0 per cent. The reaction rate at reflux temperature without agitation was higher than the reaction rate at room temperature with agitation, when chloroform was not used.

The formation of isomers was not measurably influenced by the presence of either thionyl chloride or chloroform. The melting point of the sulfonamide prepared from the product mixture of a sulfonation reaction carried out at reflux temperature was 209.5°C., indicating a high percentage of beta-naphthalenesulfonamide in the melting point sample. The melting points of the sulfonamides prepared from product mixtures of reactions carried out at room temperature and 9°C. were 138°C. and 143°C., respectively, indicating high percentages of alpha-naphthalenesulfonamide in the melting point samples. This agrees with the normal predominance of beta acids in high temperature reaction products and of alpha acids in low temperature reaction products⁽¹⁰⁾.

C. Sulfonation of Bromobenzene

The yield of bromobenzenesulfonic acid after two and one-half hours at reflux temperature was 75.4 per

cent in the presence of one mole of thionyl chloride per mole of sulfuric acid. When the amount of thionyl chloride was increased 20 per cent, the yield of the sulfonic acid was 77.2 per cent after one-half hour at reflux temperature. When agitated at room temperature for four and one-half hours in the presence of 20 per cent molar excess of thionyl chloride with respect to sulfuric acid, the yield of the sulfonic acid decreased to 33.0 per cent. Little or no sulfone formation was observed.

The presence of the thionyl chloride during the reaction did not alter the para directing nature of the bromo group, since the melting point of the sulfonamide indicated 100 per cent para-bromobenzene-sulfonic acid⁽⁶⁾.

D. Sulfonation of Ortho-bromotoluene

When a 20 per cent excess of thionyl chloride with respect to sulfuric acid was used in the sulfonation of ortho-bromotoluene, the yield of the sulfonic acid was 53.9 per cent after two and three-fourths hours at reflux temperature. After 45 minutes at reflux temperature, the yield of the sulfonic acid was 43.2 per cent. The reaction was

faster at room temperature with agitation, the yield being 60.1 per cent after two and one-fourth hours. No sulfone formation was observed.

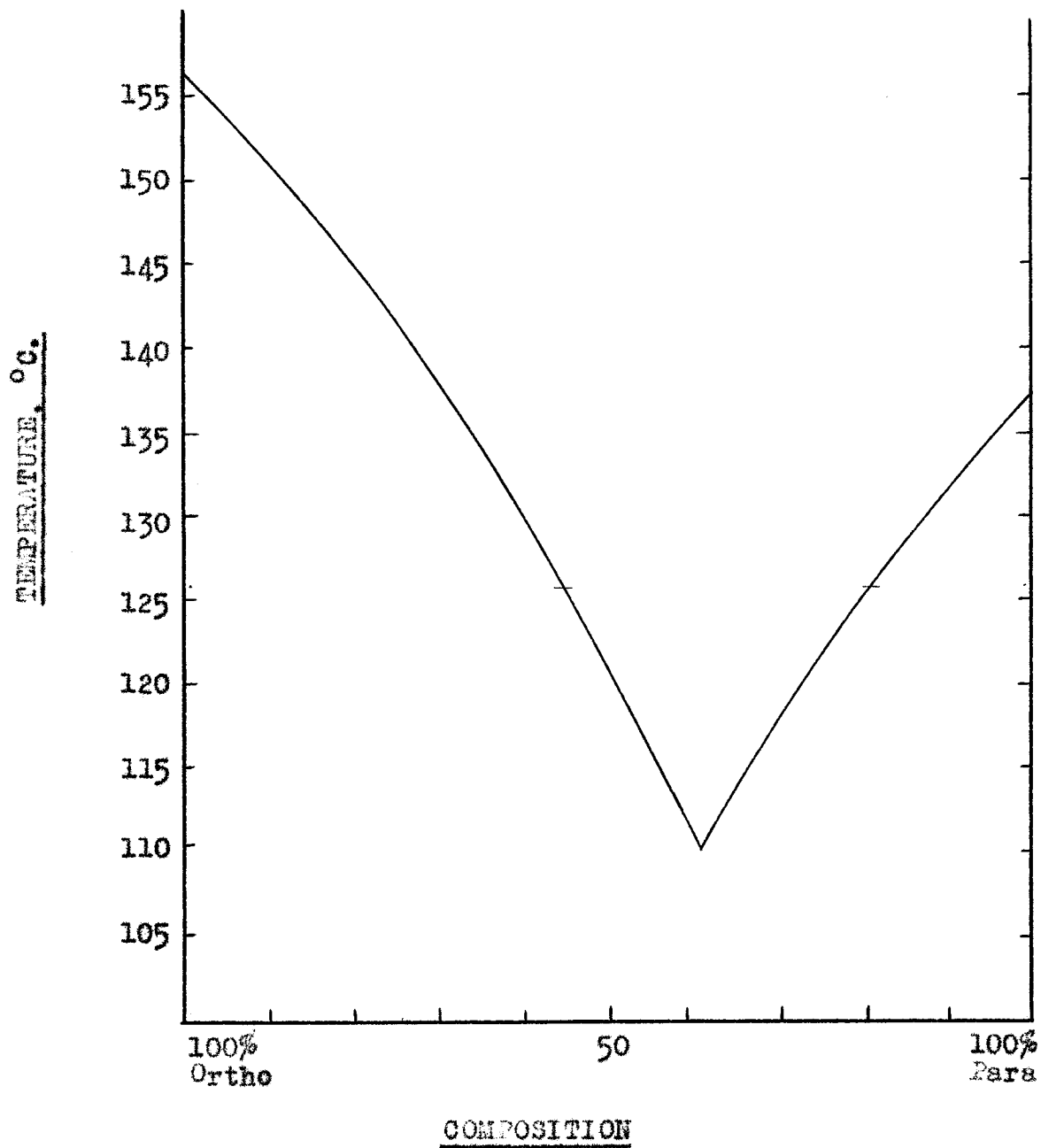
E. Sulfonation of Chlorobenzene

The yield of chlorobenzenesulfonic acid was 69.5 per cent after 15 minutes at reflux temperature in the presence of 20 per cent excess thionyl chloride with respect to sulfuric acid. When agitated at room temperature for four and one-half hours, the yield of the sulfonic acid was 87.2 per cent. A small amount of sulfone was found in the product.

The presence of the thionyl chloride did not affect the para directing nature of the chloro group, since the melting point of the sulfonamide indicated the presence of 100 per cent para-chlorobenzenesulfonic acid in the product⁽⁶⁾.

Harkins⁽⁸⁾ reported a yield of 90.5 per cent sulfonic acid after agitation for 15 minutes at reflux temperature, 90.0 per cent after three hours of agitation at room temperature followed by five hours at reflux temperature without agitation, and 85.7 per cent after five hours of agitation at room temperature. The product contained 100 per cent para-chlorobenzenesulfonic acid. Harkins' combined use of heat and

agitation accounts for the difference between his first result and the results reported in this paper. The last result is in good agreement with a similar experimental run reported in this paper.

VII. MELTING POINT CURVE

Melting point curve of mixtures of Ortho- and Para-toluene sulfonamides. (7)

VIII. LITERATURE CITED

- (1) Rây and Dey, J. Chem. Soc., 117, 1405 (1920).
- (2) Guyot, Chimie et industrie, 2, 879 (1919).
- (3) Thomas, Anziletti, and Hennion, Ind. Eng. Chem., 32, 408 (1940).
- (4) Simons, Passino, and Archer, J. Am. Chem. Soc., 63, 608 (1941).
- (5) Shriner & Fuson, "Identification of Organic Compounds", Wiley, New York, 1948, p. 216.
- (6) Ibid., p. 273.
- (7) McKie, J. Chem. Soc., 113, 799 (1918).
- (8) Harkins, thesis, Newark College of Engineering, Newark, 1954, pp. 12-14.
- (9) Ibid., pp. 16-17.
- (10) Groggins, "Unit Processes in Organic Synthesis", McGraw-Hill, New York, 1935, p. 243.