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The sulfonation of some aromatic compounds using sulfuric acid in the presence of thionyl chloride

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I

The Sulfonation of Some Aromatic Compounds Using
Sulfuric Acid In The Presence Of Thionyl Chloride

By

Hugh. H. Harkins

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF SCIENCE
With a Major in Chemical Engineering
in the
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at the
Newark College of Engineering

May 1954

II

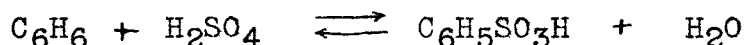
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I. INTRODUCTION

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, of course, sulfuric acid in varying concentrations and in the presence of various catalysts.

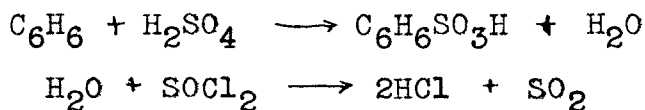
In the case of the sulfonation of benzene using sulfuric acid, the reaction is very slow at room temperature, ^{even at reflux temperature} and in fact equilibrium is reached only after 20 to 30 hours when equal volumes of benzene and sulfuric acid are reacted at reflux temperature, 80% of the benzene being used. The reaction of benzene and sulfuric acid is reversible,



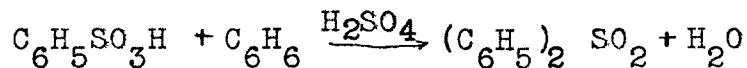
and when the water, which is formed, reduces the sulfuric acid concentration to a certain point, equilibrium is established. This concentration varies with the temperature and is defined as the π value⁽¹⁾. In order to maintain the concentration of sulfuric acid high enough for sulfonation to proceed, the water formed must be removed by some means, either

physical or chemical. The removal of the water by physical means has been performed by such means as passing the aromatic vapor through hot sulfuric acid, by distilling the water under reduced pressure, or by removing the water using an inert gas. It has been reported that the use of boron trifluoride⁽²⁾ or hydrogen fluoride⁽³⁾ facilitates sulfonation by reacting chemically with the water, thus maintaining 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:



Sulfone formation occurs to a varying extent as a side reaction according to the equation:



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

The sulfonation reactions reported are those of benzene, toluene, nitro benzene and chloro benzene.

II. EXPERIMENTAL PROCEDURE

The actual conditions of sulfonation are given with each experimental sulfonation reported. However, at the completion of each sulfonation reported, regardless of conditions of reaction, the following procedure was followed in preparing the samples for subsequent analysis:

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

B. The sulfonation mix was poured into cold water, and the remaining volatile solvent was driven off by ~~heating~~^{boiling} the aqueous solution.

C. After the aqueous solution had been allowed to cool, it was filtered ^{and washed} into a volumetric flask, and the water-insoluble [^] ~~matter filtered out,~~^{sulfone} dried and weighed. The filtrate (in the volumetric flask) was diluted to the mark with distilled water and analyzed, for the sulfonic acid ~~and~~, for the unreacted sulfuric acid, and for hydrochloric acid.

III. ANALYTICAL PROCEDURES

A. Determination of Sulfonic Acid

1. Titration Method

An aliquot portion of the water solution was taken and titrated to the phenolphthalein end point with standard sodium hydroxide. Corrections were made for hydrochloric acid and sulfuric acid present.

2. Gravimetric Method

An aliquot portion of the water solution was taken, neutralized with calcium carbonate and boiled for 15 minutes. This was immediately filtered, evaporated to dryness and kept at 105° C overnight. The dried ~~down~~ sample was weighed as the calcium salt of the sulfonic acid. Corrections were made for calcium chloride present.

B. Determination of Chlorides

When correcting for chlorides, an aliquot portion of the water solution was taken and neutralized with calcium carbonate. The chloride was then titrated with standard silver nitrate using potassium chromate as the indicator.

C. Determination of Unreacted Sulfuric Acid

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

D. Preparation of the p-toluidine Salt^(4,5)

A portion of the water solution was taken, neutralized with N/10 NaOH and dried. A two gram sample was dissolved in the minimum amount of boiling water and one gram of p-toluidine hydrochloride was added. The solution was then boiled and the crystals were then allowed to form by cooling. The product was filtered, and recrystallized from a minimum amount of boiling water. A sample of the p-toluidine salt, which had been dried under vacuum, was weighed, and the neutralization equivalent was determined by titrating with N/10 NaOH to the phenolphthalein end point. The neutralization equivalent found was then compared to the theoretical value.

E. Preparation of the Sulfonamide Derivative⁽⁴⁾

A two gram sample of the dried sodium salt of the sulfonic acid was reacted with 5 grams of PCl_5 to form the sulfonyl chloride. The amide was prepared from the sulfonyl chloride by mixing and heating with concentrated ammonia.

The reason for the preparation of the sulfonamide is primarily for the determination of its melting point, as the sulfonic acids themselves are usually too low melting for this determination. In cases where isomers are formed, the use of the melting point curve of the sulfonamides of the isomers is a method used to determine the percentage of each isomer present. If the melting point determined corresponds to two compositions on the curve, a mixed melting point may be determined using a mixture of a pure sample of one of the isomers and the experimental sample. The melting point determined this way will then indicate which of the two possible compositions is the correct one, as the mixed melting point will either be higher or lower than the original.

IV. EXPERIMENTAL RESULTS AND DATA

A. Sulfonation of Benzene

Experimental Run 1

Mole Ratios: 1 mole sulfuric acid : 10 moles benzene : 3 moles thionyl chloride.

Reaction Conditions: To a 500 ml. round-bottom flask were added 12.25 g. sulfuric acid, 98.5 g. benzene, and 59.5 g. thionyl chloride. The flask was attached to a water-cooled condenser, placed on a hot water bath, and the contents were allowed to reflux gently until the original two-phase system became homogeneous (one hour and fifteen minutes). The refluxing was continued for one more hour, at the end of which time the condenser was removed and the volatile matter removed by distilling and aspirating for a total of one hour more.

Results: Water Insoluble Matter (air dried)
M.P. 123°-124°C (Calculated as sulfone). . . 17.6%
Reacted sulfuric acid (sulfonic acid-
gravimetric) 86.4%
Unreacted sulfuric acid Nil

Experimental Run 2

Mole Ratios: 1 mole sulfuric acid : 10 moles benzene : 3 moles thionyl chloride.

Reaction Conditions: To a 500 ml. round-bottom flask were added 24.5 g. sulfuric acid, 197 g. benzene and 119 g. thionyl chloride. The procedure of Experiment 1 was then followed.

Results: Water Insoluble Matter(as sulfone) 25.8%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 72.7%
Reacted Sulfuric Acid (sulfonic acid,
titration) 71.9%
Unreacted Sulfuric Acid Nil

Preparation of para toluidine salt of
the sulfonic acid^(4,5)

N.E.(found) 265.50
N.E.(theory) 265.22

Experimental Run 3

Mole Ratios: 1 mole sulfuric acid : 1.2 moles
thionyl chloride : 3 moles benzene.

Reaction Conditions: To a 500 ml. three-necked round-bottom flask were added 58.8 g. sulfuric acid, and 140 g. benzene. To the flask were connected a water-cooled condenser, a dropping funnel, and a sealed, motor-driven stirrer. The flask was heated by an electric heating element until reflux temperature was reached, at which time 85.8 g. of thionyl chloride were added over a period of 15 minutes by

means of the dropping funnel. Refluxing was continued for one and one-half hours after the thionyl chloride had been added. After the refluxing was stopped the volatile matter was distilled off, and aspiration applied for a total of one-half hour.

Results: Water Insoluble Matter(sulfone) 1.6%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 96.1%
Reacted Sulfuric Acid (sulfonic acid,
titration) 96.3%
Unreacted Sulfuric Acid(gravimetric) . . 2.7%

Experimental Run 4

Mole Ratios: Same as Experimental Run 3.

Reaction Conditions: Same as Experimental Run 3 except that the reflux time was increased from $1\frac{1}{2}$ hours to 2 hours.

Results: Water Insoluble Matter(sulfone) 1.2%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 94.8%
Unreacted Sulfuric Acid(gravimetric). . 4.7%

Experimental Run 5

Mole Ratios: 1 mole sulfuric acid : 1.2 moles thionyl chloride : 3 moles benzene.

Reaction Conditions: To a 3-necked round-bottom flask were added 47.4 g. sulfuric acid,

71.4 g. thionyl chloride and 118 g. benzene. A thermometer, sealed agitator, and water-cooled condenser were used, and agitation was allowed to proceed at room temperature (30°C-38°C). It was noted that after four hours of agitation, the two-phase system became homogeneous, and at the end of five hours, the evolution of gas stopped. Agitation was continued for one hour after the evolution of gas ceased. The volatile matter was then aspirated for 2¼ hours at room temperature (32°C).

Results: Water Insoluble Matter(sulfone) 0.9%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 95.7%
Unreacted Sulfuric Acid(gravimetric). . 3.6%

Experimental Run 6

Mole Ratios: 1 mole sulfuric acid : 1.2 moles
thionyl chloride : 3 moles benzene.

Reaction Conditions: To a 250 ml. ground-glass Erlenmeyer flask were added 4.75 grams sulfuric acid, 7.14 grams thionyl chloride, and 11.8 grams benzene. A glass-covered magnetic pole stirring bar was inserted, a water-cooled condenser was attached, and the flask was placed over the motor so that continuous stirring took place for four hours at room temperature. The excess volatile

matter was removed by aspirating the flask for fifteen minutes.

Results: Water Insoluble Matter(sulfone) 0.1%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 90.4%

Experimental Run 7

Mole Ratios: 1 mole sulfuric acid : 0.6 moles
thionyl chloride : 3 moles benzene.

Reaction Conditions: Same as Experimental Run 6,
except that the amount of thionyl chloride was re-
duced by 50 per cent.

Results: Water Insoluble Matter Nil
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 73.1%

Experimental Run 8

Mole Ratio: 1 mole sulfuric acid : 3 moles
benzene.

Reaction Conditions: Same as Experimental Runs
6 and 7 except that no thionyl chloride was present.

Results: Water Insoluble Matter Nil
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 30.8%

Experimental Run 9

Mole Ratio: 1 mole sulfuric acid : 1.2 moles
thionyl chloride : 3 moles benzene.

Reaction Conditions: To a 250 ml. Erlenmeyer flask were added 9.4 g. sulfuric acid, 14.3 g. thionyl chloride, and 23.6 g. benzene. A water-cooled condenser was attached, and agitation using a magnetic-pole stirring bar and motor took place for $2\frac{1}{2}$ hours at room temperature. At the end of $2\frac{1}{2}$ hours the stirring was stopped and the solution was allowed to reflux gently for three hours, at the end of which time the excess volatile matter was removed by use of an aspirator.

Results: Water Insoluble Matter(sulfone) 1.1%
Reacted Sulfuric Acid (sulfonic acid,
titration) 96.2%
Unreacted Sulfuric Acid(gravimetric). 2.4%

B. The Sulfonation of Monochlorobenzene

Experimental Run 10

Mole Ratios: 1 mole sulfuric acid : 1.2 moles thionyl chloride : 3 moles monochlorobenzene.

Reaction Conditions: To a 500 ml. three-necked round-bottom flask were added 58.8 g. sulfuric acid and 202.5 g. of the chlorobenzene. A water-cooled condenser and a sealed agitator were attached to the flask and 85.8 g. of thionyl chloride were added slowly by means of a dropping funnel. Heat was applied and agitation took place while the

thionyl chloride was being added. After the addition was completed, refluxing and agitation were continued for 15 minutes, at the end of which time the volatile matter was distilled off.

Results: Water Insoluble Matter(sulfone) 1.7%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 90.5%
Unreacted Sulfuric Acid(gravimetric) . . 2.8%

Experimental Run 11

Mole Ratios: 1 mole sulfuric acid : 1.2 moles
thionyl chloride : 3 moles Monochlorobenzene.

Reaction Conditions: To a 500 ml. three-necked round-bottom flask were added 47.4 g. sulfuric acid, 71.4 g. thionyl chloride, and 168.7 g. monochlorobenzene. To the flask were attached a water-cooled condenser, a thermometer, and a sealed agitator. Agitation was allowed to take place for four hours at room temperature, at which time the two phase system became homogeneous. At the end of five hours the evolution of gas ceased, agitation was stopped, and water was added so as to steam distill the excess chlorobenzene.

Results: Water Insoluble Matter 1.4%
Reacted Sulfuric Acid (sulfonic acid,
gravimetric) 85.7%

Unreacted Sulfuric Acid(gravimetric) . . . 15.9%

Preparation of para toluidine salt of
the Sulfonic Acid⁽⁵⁾

N.E.(found) 302.07

N.E.(theory) 299.77

Experimental Run 12

Mole Ratios: 1 mole sulfuric acid : 1.2 moles
thionyl chloride : 3 moles monochlorobenzene.

Reaction Conditions: In a 250 Erlenmeyer flask
were placed 5.249 grams sulfuric acid, 7.14 g.
thionyl chloride, and 16.8 g. monochlorobenzene.
A water-cooled condenser was attached and agitation
by means of a magnetic pole stirring bar and motor
took place at room temperature until the two phase
system became homogeneous (3 hrs.). Refluxing on
a steam bath then took place for another four hours.
The excess volatile matter was removed by means of
an aspirator.

Results: Water Insoluble Matter(sulfuric) 1.6%

Reacted Sulfuric Acid(titration) 90.0%

Unreacted Sulfuric Acid(gravimetric) 8.4%

Preparation of the sulfonamide
derivative M.P. = 144°C⁽⁶⁾

C. The Sulfonation of Nitro Benzene

Experimental Run 13

Mole Ratios: 1 mole sulfuric acid : 1.2 moles thionyl chloride : 3 moles nitrobenzene.

Reaction Conditions: In a 500 ml. three-necked round bottom flask were placed 24.5 g. sulfuric acid, 35.7 g. thionyl chloride, and 92.3 g. nitrobenzene. A condenser and thermometer were inserted and agitation was allowed to take place for three hours at room temperature using a mercury sealed stirrer. The solution was at all times homogeneous. At the end of the run, the excess nitrobenzene was removed by steam distillation.

Results: Unreacted Sulfuric Acid (gravimetric) 99.1%

Experimental Run 14

Mole Ratios: 1 mole sulfuric acid : 1.2 moles thionyl chloride : 3 moles nitrobenzene.

Reaction Conditions: In a 250 ml. Erlenmeyer flask were placed 10.62 g. sulfuric acid, 14.3 g. thionyl chloride and 37.0 g. nitrobenzene. A condenser was attached and the homogeneous solution was heated to about 70° C and allowed to remain at that temperature for 10 hours. The excess volatile matter was removed by aspiration.

Results: Reacted Sulfuric Acid (sulfonic acid, titration) 6.2%
Unreacted Sulfuric Acid (gravimetric) . . 93.2%

D. Sulfonation of Toluene

Experimental Run 15

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

Reaction Conditions: To a three necked 500 ml. round-bottom flask were added 24.5 g. sulfuric acid, 35.7 g. thionyl chloride, and 69 g. toluene. A water-cooled condenser and thermometer were attached to the flask. The mixture was agitated by a mercury sealed stirrer at room temperature for a period of four hours. The excess toluene was steam distilled.

Results: Water Insoluble Matter Nil
Reacted Sulfuric Acid (sulfuric acid, gravimetric) 87.5%
Unreacted Sulfuric Acid (gravimetric) . . . 5.3%

Experimental Run 16

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

Reaction Conditions: In a 250 ml. Erlenmeyer flask were placed 5.25 g. sulfuric acid, 7.14 g. thionyl chloride and 13.9 g. toluene. The flask was attached to a reflux condenser and agitation

was allowed to take place at room temperature until the solution became homogeneous ($\frac{1}{2}$ hr.). A magnetic pole stirring bar and motor were used for stirring. The solution was then heated to about 70°C for 3 hours, at the end of which time the excess volatile matter was removed by aspirating for one half hour.

Results: Water Insoluble Matter Nil
Reacted Sulfuric Acid (sulfonic acid,
titration) 91.3%
Unreacted Sulfuric Acid(gravimetric). 8.7%

Experimental Run 17

The same mole-ratios and reaction conditions hold true for this run as for Run 16.

Results: Water Insoluble Matter Nil
Reacted Sulfuric Acid (sulfonic acid,
titration) 94.0%
Unreacted Sulfuric Acid(gravimetric). 3.0%
Preparation of Sulfonamide deriva-
tive M.P.= 134° - 135° C

V. SUMMARY

RUN	REACTANTS (MOLES)			YIELD (PERCENT)			CONDITIONS
	Aromatic Compound	Sulfuric Acid	Thionyl Chloride	Sulfonic Acid	Sulfuric Acid	Sulfone	
1. Benzene	10.00	1.00	3.00	86.4	nil	17.6	Reflux, 1.25 hrs.
2. Benzene	10.00	1.00	3.00	72.7	nil	25.8	Reflux, 1.25 hrs.
3. Benzene	3.00	1.00	1.20	96.3	2.7	1.6	Reflux, 1.5 hrs.
4. Benzene	3.00	1.00	1.20	94.6	4.7	1.2	Reflux, 2.0 hrs.
5. Benzene	3.00	1.00	1.20	95.7	3.6	0.6	30°-33°C., 5.5 hrs.
6. Benzene	3.00	1.00	1.20	90.4	-	0.1	Room temp., 4 hrs.
7. Benzene	3.00	1.00	0.60	73.1	-	nil	Room temp., 4 hrs.
8. Benzene	3.00	1.00	0.00	30.8	-	nil	Room temp., 4 hrs.
9. Benzene	3.00	1.00	1.20	96.2	2.4	1.1	Reflux, 3 hrs.
10. Chlorobenzene	3.00	1.00	1.20	90.5	2.8	1.7	Reflux, 15 mins.
11. Chlorobenzene	3.00	1.00	1.20	85.7	15.9	1.4	Room temp., 5 hrs.
12. Chlorobenzene	3.00	1.00	1.20	90.0	8.4	1.6	Reflux, 4 hrs.
13. Nitrobenzene	3.00	1.00	1.20	-	99.1	-	Room temp., 3 hrs.
14. Nitrobenzene	3.00	1.00	1.20	6.2	93.2	-	70° C., 10 hrs.
15. Toluene	3.00	1.00	1.20	87.5	5.3	nil	Room temp., 4 hrs.
16. Toluene	3.00	1.00	1.20	91.3	8.7	nil	70° C., 3 hrs.
17. Toluene	3.00	1.00	1.20	94.0	3.0	nil	70° C., 3 hrs.

VI. CONCLUSIONS

A. Sulfonation of Benzene

It may be observed that the presence of thionyl chloride facilitates the sulfonation of benzene when used in slight molar excess with respect to the sulfuric acid. A ratio of 10 moles benzene : 1 mole sulfuric acid, in the presence of thionyl chloride will react quantitatively when refluxed for as little as $2\frac{1}{4}$ hours. However, in carrying out the reaction using such a large excess of benzene, the phenyl sulfone formed amounts to 17--26%. By reducing the ratio to 3 moles benzene : 1 mole sulfuric acid, the sulfone formed is reduced to 1--2% when refluxing takes place for from $1\frac{1}{2}$ --3 hours, the sulfonic acid being formed in the amount of 95--97%. At room temperature the benzene sulfonic acid is formed in the amount of 96% if the reaction is carried out for 6 hours.

The amount of thionyl chloride present affects the completeness of the reaction, as when 1.2 moles thionyl chloride : 1 mole sulfuric is present, a 90.4% sulfonation of benzene takes place (4 hrs., room temp.). A 0.6 mole thionyl chloride : 1 mole sulfuric acid ratio reduces the completeness of reaction to 73% and in the absence of thionyl chloride only 31% of the sulfuric

acid reacts to form the benzene sulfonic acid.

B. Sulfonation of Monochlorobenzene

The sulfonation of chlorobenzene at room temperature yielded 86% sulfonic acid and by reacting at a temperature of as high as 80° C, a yield of only 90% was obtained. The presence of the thionyl chloride during the reaction did not alter the para directing nature of the chloro group as the M.P. of the sulfonamide indicated 100% para chlorobenzenesulfonic acid.

C. Sulfonation of Nitrobenzene

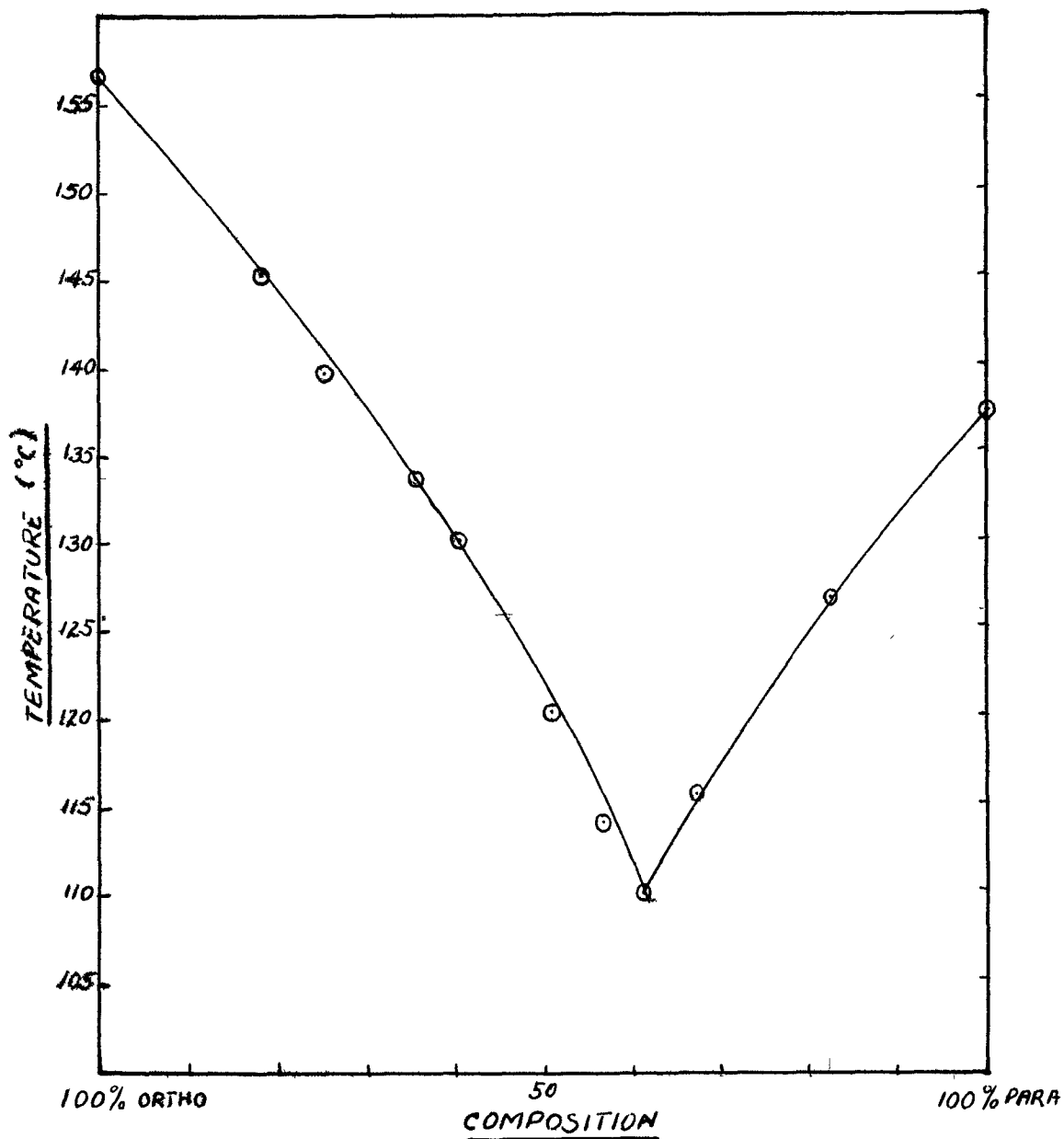
The presence of thionyl chloride was of no real value in the sulfonation of nitrobenzene. It was shown that at room temperature 99% of the sulfuric acid remained unreacted and a 10 hr. reaction at 70° C left 93% of the sulfuric acid unreacted. This is due, of course, to the fact that nitrobenzene is normally an extremely inert substance. It can be sulfonated only by the use of oleum at a high temperature.

D. Sulfonation of Toluene

The presence of thionyl chloride results in an 88% yield of toluenesulfonic acid when reacted for only four hours at room temperature. By increasing the temperature to 70° for three hours a yield of 91--93% sulfonic acid was obtained. The melting point of the

sulfonamide (134--135° C) indicated the presence of isomers. A mixed melting point determined with p-toluene sulfonamide indicates the presence of high para rather than high ortho toluenesulfonamide. The composition as shown by the melting point curve (7) indicates the presence of 95% para-toluenesulfonamide. Since the para isomer is ordinarily formed in larger amounts at higher temperatures, the presence of the thionyl chloride had no measurable influence upon the percentages of isomers formed.

VII. MELTING POINT CURVE



MELTING POINT CURVE OF MIXTURES OF ORTHO TOLUENE AND
PARA TOLUENE SULFONAMIDES. (7)

VIII. LITERATURE CITED

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