I. CERTAIN AZO DYES DERIVED FROM 2 - AMINO PHENOL - 4 - SULFONIC ACID

II. A STUDY OF THE REDUCTION RATE OF 2 - NITRO PHENOL - 4 - SULFONIC ACID

BY

ALBERT E. COHEN

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

1953

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

____

____

NEWARK, NEW JERSEY
JUNE, 1953

ACKNOWLEDGMENTS

Particular acknowledgment is made to Professor James A. Bradley for his suggestions and guidance in the preparation of this thesis.

I wish, also, to express my indebtedness to my wife, Marion, for her valuable assistance in the preparation of this manuscript.

CONTENTS

TABLES

PART I

PRECOPPERED AZO DYESTUFFS FOR COTTON

INTRODUCTION

Considerable commercial interest in precoppered azo dyestuffs suitable for dyeing cotton has been shown, as these products are, in general, markedly superior to uncoppered dyestuffs, with respect to light and wash fastness.

Some information concerning the German work on precoppered dyestuffs for cotton is available in the Fiat Reports. (1) The work indicated in this report was stated to be with ortho, ortho'-dimethoxy-azo or ortho-hydroxy, ortho'-methoxy-azo containing dyestuffs of the water soluble type. The reference cited above refers also to another Fiat Report known as the Robitschek Report, (2) for examples of precoppered cotton dyes. It was found here that in addition to the above types of azo dyes, an ortho, ortho'-dihydroxy-azo-containing dye was coppered. The example referred to is the product of 2 - aminophenol - 4 - sulfonic acid, coupled to resorcin, which was subsequently coppered. However, this is not substantive to cotton, but it is used in a substantive dyestuff by recoupling it on one

---

1. Fiat Final Report No. 1313, German Dyestuffs and Dyestuff Intermediates, 1 February 1948, Dept. of Commerce, Office of Technical Services, PB 85172, Vol. III, Pg. 204

2. Fiat Final Report No. 764, Dyestuff Manufacturing Processes of I. G. Farbenindustrie, A G, 18 April 1947, Dept. of Commerce, Office of Technical Services, PB 74026, Pg. 2297, PB 74025, Pg. 1690

arm of tetrazo benzidine, while salicylic acid is coupled on the other arm of tetrazo benzidine.

A search through Chemical Abstracts indicates that there are other cases where 2 - aminophenol - 4 - sulfonic acid is diazotized and coupled to naphthol or phenol derivatives yielding dyes which can be precoppered. (3) Since the ortho, ortho'-dihydroxy-azo combination has been shown to have been sucessfully metallized, it is of great interest, since there are many naphthol derivatives and phenol derivatives which, when coupled to 2 - aminophenol - 4 - sulfonic acid, yield the ortho, ortho'-dihydroxy-azo combination.

It was throught that J acid derivatives would be worthwhile products for coupling to 2 - aminophenol - 4 - sulfonic acid, since these derivatives contain a combination of hydroxy and sulfonic acid groups which direct the coupling to a position ortho to the hydroxy group. Furthermore, J acid and its derivatives, coupled ortho to the hydroxy group, usually result in substantive cotton dyes. (4) Such azo dyes could reasonably be expected to form coppered dyes for cotton, since they would have the ortho, ortho'-

---

3. Chemical Abstracts, <u>1949</u>, 44741, 5598h

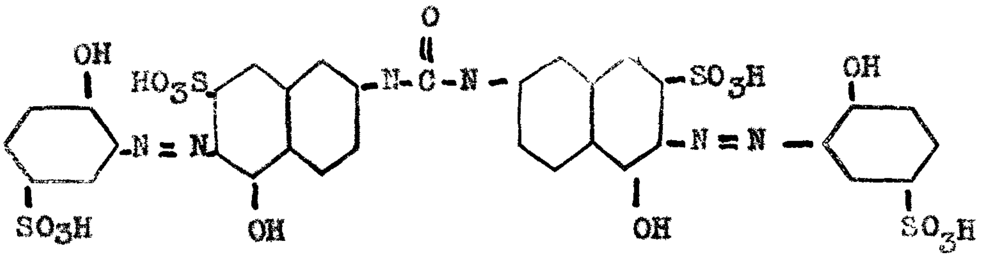
4. Fieser and Fieser, Organic Chemistry, 1st Edition, 1944
D. C. Heath and Company, Boston, Massachusetts, Pg. 863

dihydroxy-azo combination and would also have the substantivity to cotton imparted by J acid derivatives. Accordingly, coppered compounds of the following couplings were prepared:

1. 2 - aminophenol - 4 - sulfonic acid coupled to urea J acid.
2. 2 - aminophenol - 4 - sulfonic acid coupled to phenyl J acid.
3. 2 - aminophenol - 4 - sulfonic acid coupled to m-amino benzoyl J acid.

EXPERIMENTAL

Coupling of 2-Aminophenol - 4 - Sulfonic Acid to Urea J Acid



Diazotization of 2-aminophenol - 4 - sulfonic acid.

A 600 cc. beaker was set in an ice bath and fitted with a thermometer and a mechanical agitator. In this the following were slurried:

180 g. water

16.4 g. 2 - aminophenol - 4 - sulfonic acid (20 g. 82% material) and

18 g. hydrochloric acid 19.5° Be.

A light tan slurry resulted. Ice was then added to the ice bath, cooling the slurry to 12° C. at which time

6 g. sodium nitrite, dissolved in

20 g. water, were added dropwise over a period of five minutes. The temperature was held in the range 12° - 15° C. by portion-wise addition of

12 g. ice. The material goes into solution as diazotization progresses and its appearance is dark brown in the beaker and yellow when spotted on

filter paper. A faint but definite end point on potassium iodide starch paper was maintained one-half hour. The final volume was 130 cc.

Urea J acid solution. A 1000 cc. beaker was set in an ice bath and fitted with a thermometer and a mechanical agitator. In this the following were slurried:

100 g. water

23.8 g. urea J acid (85 grams of 28.0% material based on a molecular weight of the disodium salt, 548). This slurry was heated to 55° C. To this were added a total of

4.5 g. sodium hydroxide (50% solution) until the reaction, when spotted on Brilliant Yellow Indicator Paper, was faint orange. A clear solution was noted at this point and

8 g. sodium carbonate were added. The solution was cooled to 10° C. by addition of ice to the ice bath.

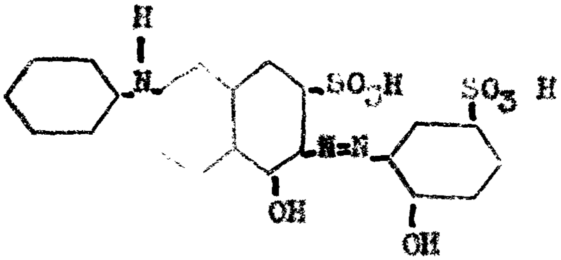
Coupling. The diazo compound was added slowly to the urea J acid solution. The color of the material in the beaker became violet almost immediately. At first a spot of the reaction mixture, when spotted with neutral H acid solution, gave a negative test, indicating rapid consumption of the diazo compound. In approximately one-half

hour the addition of diazo compound was complete and it was noted that a spot of the mixture, when spotted with neutral H acid solution, gave a positive test. However, less than a minute later this test was negative, indicating that all of the diazo solution had reacted. At this point the temperature was 14° C. and the solution was very viscous. An additional
200 g. water were added over a period of one hour with no apparent decrease of viscosity. The coupled material was allowed to stir without temperature control for twenty hours at which time there was no apparent change. The pH of the coupled material was approximately 8. The volume was 600 cc. It was noted by spotting on filter paper that some of the material was still in solution.

Isolation. The reaction product was heated to 60° C. at which point the viscosity appeared greatly reduced while the solubility had increased markedly. To this a total of
200 g. sodium chloride was added. At this point it was noted that the amount of precipitated dyestuff had increased, but that considerable dyestuff was still in solution. To this mixture
6 g. hydrochloric acid 19.5° Be. were added. It was noted that almost all of the dyestuff was pre-

cipitated. The color of the mixture had turned from violet to red and its pH was approximately 5.6. This material was then filtered in a 17.5 cc. Buechnor funnel. The filtration was slow. The cake weight was 361 grams. The cake was dried at 900 C. for 28 hours. Its dry weight was 123.6 grams. It was then pulverized in preparation for metallization.

Coupling of 2-Aminophenol - 4 - Sulfonic Acid to Phenyl J Acid



Diazotized 2 - aminophenol - 4 - sulfonic acid. For this coupling, the 2 - aminophenol - 4 - sulfonic acid was diazotized in the same manner as for the coupling of urea J acid (page 4).

Phenyl J acid solution. A 1000 cc. beaker was set in an ice bath and fitted with a thermometer and a mechanical agitator. In this the following were slurried:

150 g. water and

50.1 g. phenyl J acid (55.4 grams 90% material, molecular weight 315). To this were added

9 g. 50% sodium hydroxide. At this point the reaction on Brilliant Yellow Indicator Paper was faint orange and the material was completely dissolved. To this solution

8 g. sodium carbonate were added. The solution was cooled to 10° C. by the addition of ice to the ice bath.

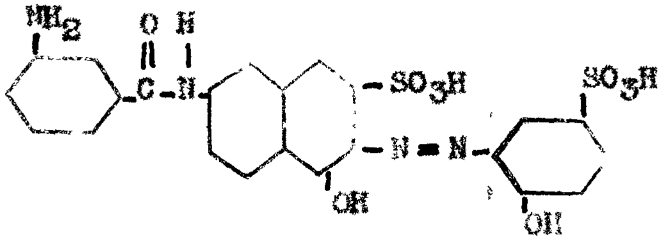
Coupling. The diazo solution was added slowly to the phenyl J acid solution. The color of the material became violet almost immediately. Spotting with neutral H acid solution indicated that the diazo compound was consumed almost immediately. In approximately one-half hour all of the diazo compound had been added and it was noted that the material was very viscous. The pH was approximately 8 and the temperature was 14° C. Spotting with neutral H acid solution gave a negative test, indicating complete coupling of the diazo compound. The volume was approximately 475 cc. and the material was only partly precipitated. After stirring twenty-two hours there appeared to be no significant change in the coupled product.

Isolation. The material was then heated to 80° C. A marked increase in the solubility was noted by spotting on filter paper. A total of

130 g. sodium chloride was added which reduced the solubility considerably. Then a total of

10 g. hydrochloric acid were added. The material changed color from violet to red. The pH dropped to 2. The solubility was reduced markedly so that only a faint tinge of soluble color was noted when spotted on filter paper. This material was then filtered in a 17.5 cc. Buechner funnel. This filtration was rapid. The cake weight was 174.5 grams. This cake was dried at 90° C. for twenty-two hours. Its dry weight was 115.2 grams. It was then pulverized in a mortar in preparation for metallization.

Coupling of 2 - Aminophenol - 4 - Sulfonic Acid to Meta Aminobenzoyl J Acid



Diazotized 2 - aminophenol - 4 - sulfonic acid. For this coupling, the 2-aminophenol - 4 - sulfonic acid was diazotized in the same manner as for the coupling of urea J acid (page 4).

Meta aminobenzoyl J acid solution. A 1000 cc. beaker was set in an ice bath and fitted with a thermometer and a mechanical agitator. In this the following were slurried:

150 g. water and

34.2 g. m aminobenzoyl J acid (90 grams 38.0% material, molecular weight 358). To this were added a total of

9 g. 50% sodium hydroxide at which point the reaction on Brilliant Yellow Indicator Paper was faintly orange. To this were added

8 g. soda ash. The mixture was cooled to 10° C. by adding ice to the ice bath.

__Coupling.__ The diazo solution was added slowly to the m aminobenzoyl J acid solution. The mixture turns violet almost immediately. Spotting with neutral H acid solution indicated that the diazo compound was consumed almost immediately. The mixture became very viscous as the coupling proceeded and in one-half hour, when all of the diazo solution had been added, the mixture was extremely viscous. Spotting with neutral H acid indicated that the diazo compound was totally reacted. The pH of the product was 8 while the temperature was 15° C. To this was added a total of

200 g. water which resulted in a slightly less viscous product. This was stirred twenty-two hours at which time no significant change was noted. The

volume at this time was approximately 600 cc.

Isolation. The reaction product was heated to 60° C., resulting in a more soluble and less viscous mixture. To this were added

150 g. sodium chloride which precipitated a portion of the dyestuff. To this were added

5 g. muriatic acid 19.5° Be. The color of the mixture became red and was well precipitated. The material was highly viscous. This was filtered in a 17.5 cc. Buechner funnel. The filtration was slow yielding a wet cake of 440 grams. The cake was dried at 90° C. for thirty-eight hours. It was then pulverized in preparation of metallization. The dry material weighed 143.0 grams.

Process for the Coppering of the Dyestuffs

From each of the coupled products two grams were reserved for dye tests.

In a one liter Erlenmeyer flask

65.4 g. copper sulfate pentahydrate were slurried with
500 g. water and
90 g. ammonia solution 26° Be.

The copper sulfate was dissolved by rapid agitation. The resulting solution contains the tetrammonia cupric ion. This solution is deep blue.

It was divided into three parts. The dried powders from the couplings were then stirred thoroughly into the tetrammonia cupric ion solution to form viscous pastes. These were transferred to shallow plates and were dried at 95 - 100° C. for twenty-six hours. The resulting product was then pulverized in preparation for the dye tests. The yields are shown in Table I.

TABLE I

COPPERED PRODUCT YIELDS

Products	Yields
Coppered product of the urea J acid coupling	142.2 g.
Coppered product of the phenyl J acid coupling	137.7 g.
Coppered product of the m aminobenzoyl J acid coupling	162.7 g.

It should be noted that the coupled diazo dyestuffs were isolated by salt addition, and thus the products contain inorganic salts which were carried over to the coppered products. Thus the relative weights do not accurately measure the yields but should roughly contain the same total number of mols of 2 - aminophenol - 4 - sulfonic acid coupled to the respective J acid derivatives. This factor was taken into consideration when the products were dyed.

Procedures for Dyeing

One gram portions of the synthesized dyestuffs, both coppered and uncoppered were dissolved in hot water and each was brought to a total volume of 1000 cc. in a volumetric flask.

For each dyeing the number of cubic centimeters taken for dyeing from the respective 1000 cc. volumetric flask, as shown in Table II, is equal to twice the number of grams of yield in each case. Thus each dye beaker contained approximately the same number of moles of coupled 2 - aminophenol - 4 - sulfonic acid.

TABLE II

QUANTITIES OF DYESTUFF USED FOR DYEING

J Acid Derivative	CC. of Uncoppered Dye	CC. of Coppered Dye
Urea J Acid	247	284.4
Phenyl J Acid	230.4	275.4
Meta Aminobenzoyl J Acid	286	325.4

The dye beakers used were of the conventional 600 cc. type. The total volume in each beaker was brought to 300 cc. The beakers were then placed in a water bath containing boiling water and the temperature inside the beakers rose to 93° C. Two ten-gram cotton skeins were inserted in each beaker and were turned constantly. In twenty minutes, 10 cc. of a 15% Glauber Salt solution was added to each beaker and again twenty minutes later. After an additional twenty minutes the skeins were then removed from the dye beakers, rinsed in cold water and dried at room temperature.

Appraisal of Substantivity and Wash-Fastness

The individual beakers were examined for the amount of color not exhausted by the skeins at the completion of dyeing. A poor exhaust is indicative of poor substantivity. No comparisons were made as it was difficult to guage the intensity of the remaining solutions because of color differences. However, they all appeared poor in this test as shown in Table III.

One skein from each dye bath was immersed in water at 55° C. in individual beakers, maintained at 55° C. by immersion in a water bath. These skeins were turned for ten minutes at which time they were removed. An indication of the wash fastness is the amount of color bled from the skeins. The comparisons shown in the following table are between coppered and uncoppered dye for the respective J acid derivative. It can be seen in Table III that each coppered dye appeared to have better wash fastness than its respective uncoppered dye.

TABLE III

PROPERTIES OF THE SYNTHESIZED DYESTUFFS

Product	Color	Exhaust	Wash
Urea J Acid coupling	scarlet	poor	poor
Urea J Acid coupling coppered	pink	poor	poor
Phenyl J Acid coupling	pink	poor	poor
Phenyl J Acid coupling coppered	blue-violet	poor	fair
Meta Aminobenzoyl J Acid coupling	scarlet	poor	poor
Meta Aminobenzoyl J Acid coupling coppered	Pink	poor	fair

Appraisal of Light Fastness

From examination of the intensity of the colors on the cotton, it appears that the urea J acid couplings, both coppered and uncoppered, while not good, are nevertheless superior to the corresponding phenyl J acid coupling products and to the corresponding m aminobenzoyl J acid coupling products. The urea J acid coupling products were selected, therefore, for light fastness tests in the Fadeometer. (5) The results of this test indicate that

---

5. Technical Manual and Year Book of the American Association of Textile Chemists and Colorists, Vol. XXVIII, 1952, Howes Publishing Company, Inc., New York, New York Pg. 100 - 103.

the coppered dyestuff showed slight fading after fifty-six hours in the Fadeometer while the uncoppered dyestuff showed strong fading after twelve hours in the Fadeometer.

CONCLUSION

The results of the experimental work show that the three azo dyes synthesized by coupling diazotized 2 - aminophenol - 4 - sulfonic acid to urea J acid, phenyl J acid, and m aminobenzoyl J acid undergo radical changes when reacted with tetrammonia cupric ion solution.

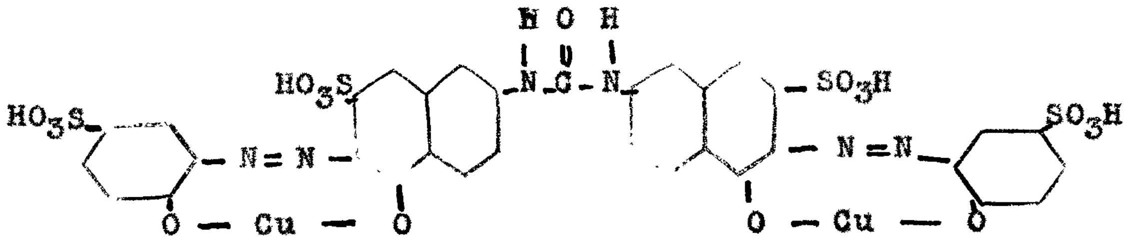
The shades of the coppered dyestuffs on cotton were bluer than the shades of the respective uncoppered products. It was found that the wash fastness of each of the coppered dyestuffs was slightly better than the wash fastness of the corresponding uncoppered dyestuff.

A very substantial improvement was noted in the light fastness properties. The coppered urea J acid derivative appeared to be four and one-half times as resistant to fading in light as the uncoppered urea J acid derivative.

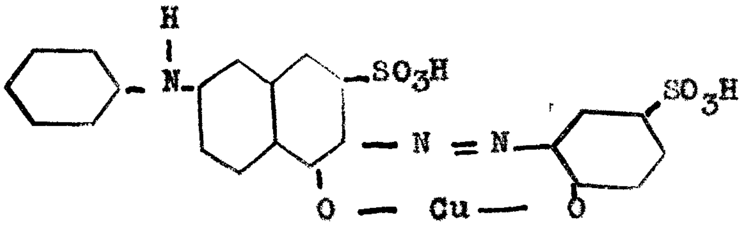
In all cases the substantivity to cotton was not judged to be satisfactory. None of the products exhausted well and deep shades were not readily obtainable. However, the urea J acid derivative was markedly more substantive to cotton than the derivatives of phenyl J acid and m aminobenzoyl J acid.

From comparison with work done by the German Dye industry, (6) it is believed that the metallized products are salts of copper having the following configurations:

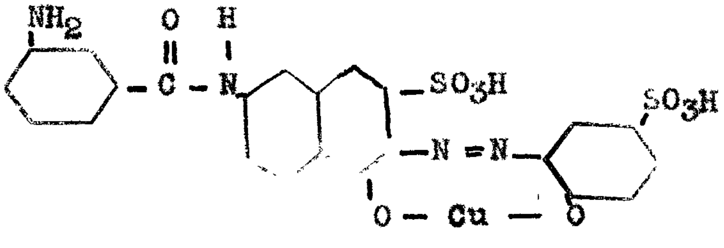
Coppered urea J acid product.



Coppered Phenyl J acid product.



Coppered m Aminobenzoyl J acid product.



---

6. (1) P. 205

COLOR CARD

<u>Uncoppered</u> | <u>Coppered</u>

2 - Aminophenol - 4 - sulfonic acid coupled to Urea J acid.

2 - Aminophenol - 4 - sulfonic acid coupled to Phenyl J acid.

2 - Aminophenol - 4 - sulfonic acid coupled to m Aminobenzoyl J acid.

PART II

THE REDUCTION RATE OF 2 - NITROPHENOL 4 - SULFONIC ACID WITH SODIUM SULFIDE

INTRODUCTION

The production of 2 - aminophenol - 4 - sulfonic acid is of considerable interest to the dyestuff industry. References in Chemical Abstracts indicate that it finds much use as an intermediate in dyestuff synthesis. (1)

This investigation is concerned mainly with the reduction rate of 2 - nitrophenol - 4 - sulfonic acid. This type of reaction finds wide application, since the preparation of primary amines by the sodium sulfide reduction of corresponding aromatic nitro compounds is an important method of laboratory and commercial synthesis. (2)

Bullock and Forbes (3) have studied the formation of sodium thiosulfate resulting as a product of the sodium sulfide reduction of aromatic nitro compounds. While the particular compound being investigated was not treated in the above cited reference, the reference was found valuable since some of the procedure used to investigate the reduction rate of 2 - nitrophenol - 4 - sulfonic acid

---

1. Chemical Abstracts - see References page 33.

2. Groggins, Unit Processes in Organic Chemistry, 3rd Edition, 1947, McGraw Hill Book Co., New York, N. Y., Pg. 94, 95, 112.

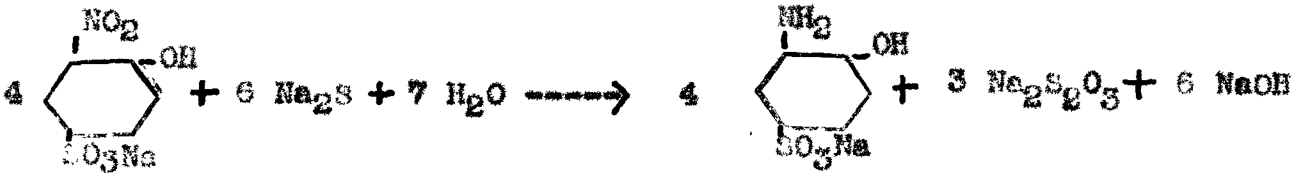
3. Bullock and Forbes, The Formation of Sodium Thiosulfate from the Oxidation of Sodium Sulfides by Means of an Aromatic Nitro Compound, Journal American Chemical Society, 55 1933, p. 232

is adapted from the procedure of Bullock and Forbes. The general equation for the reaction is given by

$$4\ RNO_2 + 6\ Na_2S + 7\ H_2O \longrightarrow 4\ RNH_2 + 3\ Na_2S_2O_3 + 6\ NaOH$$

The above equation is an overall equation for the reaction, and it is probable that the final products are a result of consecutive reactions. Bullock and Forbes found that consistent values for reaction velocity constants could be obtained by applying the bimolecular formula for different concentrations of the oxidizing agent and the total sulfide ion. (4) This indicates the rate determining reaction is one of second order.

The overall equation for the reaction being studied here is given by:



---

4. 3 p.236

EXPERIMENTAL

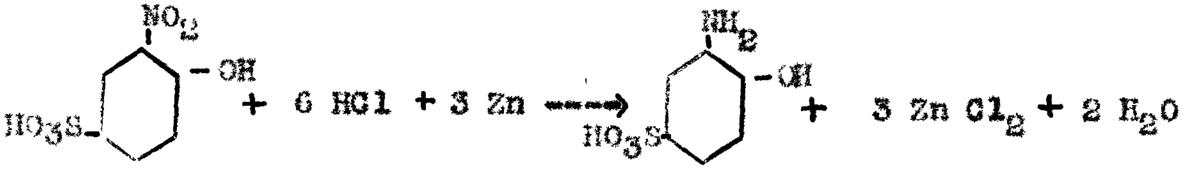
Purification of Raw 2 - Nitrophenol - 4 - Sulfonic Acid

Raw, unpurified 2 - nitrophenol - 4 - sulfonic acid was supplied to the author by the thesis sponsor. It appeared to contain considerable moisture and it was believed that there were inorganic salts present. The following is the laboratory procedure used in obtaining a product of higher purity.

In a four liter beaker the following were added:
650 g. raw 2 - nitrophenol - 4 - sulfonic acid and
3000 g. water. The material was stirred by means of a mechanical agitator and brought to a boil. At this point the temperature was 101.5° C. and the pH was approximately 3.5. A slight amount of undissolved material remained and an addition of
200 g. water was necessary to affect complete solution. The final volume was approximately 3500 cc. The temperature of this solution was brought to 5° C. by inserting the beaker in a bath containing an ice and salt mixture. At 5° C. the material was well precipitated and the mixture was filtered in a 17.5 Buechner funnel. The cake was dried at 80° C. for 30 hours and gave a product consisting of pale yellow lumps which were pulverized easily

with mortar and pestle. This material was mixed well and stored in a wax-sealed glass jar.

Analysis of Purified 2 - Nitrophenol - 4 - Sulfonic Acid



The content of 2 - nitrophenol - 4 - sulfonic acid in the product purified above was found by reducing the nitro group with zinc and hydrochloric acid (5) and then titrating the resulting amine with a standardized sodium nitrite solution. (6) The following is the procedure used:

To a 1000 cc. beaker equipped with mechanical agitation and with a thermometer, the following were added:

10.95 g. purified 2 - nitrophenol - 4 - sulfonic acid and

250 g. water. The mixture was stirred a short while and gave a yellow solution to which was added

---

5. 2 p. 77

6. Fierz-David and Blangey, Fundamental Processes of Dye Chemistry, 5th Edition, 1949, Interscience Publishers, Inc., New York, N. Y. P. 385, 386.

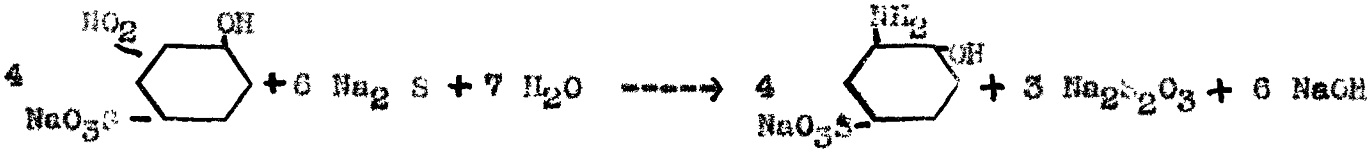
60 g. hydrochloric acid 19.5° Be. and

14.73 g. zinc dust (50% excess over theory). The temperature of this reaction was maintained at 15° C. by the addition of ice. The solution lightened in color as soon as the zinc was added. When the solution became water white, the reaction was allowed to continue twenty minutes longer during which time an evolution of gas from the surface of the zinc was noted. This product was filtered through a Buechner funnel to separate the remaining zinc particles. Analysis by titration with .92 Normal sodium nitrite was begun at once. (6) A total of 44.7 cc. .92 Normal sodium nitrite were needed in this titration. Basing the calculations on the molecular weight of the anhydrous sodium salt, it was found that the material contained 90.5% sodium salt of 2 - nitrophenol - 4 - sulfonic acid.

$$\frac{44.7}{1000} \times .92 \times \frac{241.1}{10.95} \times 100 = 90.5\%$$

The same procedure was repeated except that the reduction step was carried at 85° C. The same percentage purity was obtained by this procedure.

Sodium Sulfide Reduction of 2 - Nitrophenol - 4 - Sulfonic Acid



Two experimental runs were made. The first, Series I, was carried out at 95° C. while the second, Series II, was carried out at 63° C.

The following is the procedure used:

Stock solutions for each run were made and are listed below.

1. 500 cc. total volume of solution at 95° C. containing

   (a) .05 mol sodium salt of 2 - nitrophenol - 4 - sulfonic acid (13.35 g. of 90.5% material)

   (b) .1 mol sodium hydroxide (4 grams C.P. material)

2. 500 cc. total volume of solution at 95° C. containing .08 sodium sulfide pentahydrate (13.55 grams of C.P. material).

3. 500 cc. total volume of suspension at room temperature containing .08 mol cadmium carbonate (13.80 grams of C.P. material).

In performing the experiment, 500 cc. Erlenmeyer flasks, each containing 50 cc. of solution 1 and 50 cc. of solution 2 were immersed in a boiling water bath. The temperature of the reduction was 95° C. After various time intervals, 50 cc. of suspension 3 were added to precipitate the remaining sulfide ion as cadmium sulfide, thus preventing further reduction. The resulting mixture was then cooled in an ice bath at 5° C. and filtered, thus removing the precipitated cadmium sulfide. The filtrate was then treated with 4.5 cc. of the hydrochloric acid, 19.5° Be. and boiled to expel any hydrogen sulfide or sulfur dioxide, the latter being formed on the decomposition of acidified sodium and cadmium thiosulfates. The resulting solution was cooled with ice to 15° C. and titrated with standardized .46 Normal sodium nitrite to determine the quantity of 2 - aminophenol - 4 - sulfonic acid present.

Series II was performed similarly to Series I, except that solution 1 and solution 2 were preheated to 63° C. and the Erlenmeyer flasks in which the reactions took place were placed in an electric oven in which the temperature was maintained at 63° C. The results of the titration to determine the amount of amine formed in the reduction are given in Table IV.

TABLE IV

MOLS OF AMINE FORMED BY SODIUM SULFIDE REDUCTION OF 2 - NITROPHENOL - 4 - SULFONIC ACID AT VARIOUS TIME INTERVALS

Series I - 95° C.

Run No.	Reaction Time (Minutes)	CC. Nitrite (.46 Normal)	Moles Amine formed
1	4	0.7	0.00032
2	10	1.4	0.00064
3	20	3.4	0.0016
4	40	6.0	0.0028
5	60	7.1	0.0032
6	100	9.5	0.0044
7	140	10.0	0.0046
8	180	10.7	0.0049
9	210	10.8	0.0050

Series II - 63° C.

Run No.	Reaction Time (Minutes)	CC. Nitrite (.46 Normal)	Moles Amine formed
1	15	.2	0.000092
2	80	.7	0.00032
3	835	1.3	0.00060
4	1345	1.5	0.00069
5	2355	2.6	0.0012
6	2750	2.9	0.0013
7	3715	2.9	0.0013

The reaction in Series II appeared to come to a halt before all the nitro compound was reduced to amine. In addition, it was noted that in run No. 7, the cadmium chloride did not precipitate any yellowish cadmium sulfide, indicating consumption of the sulfide ion. It is suggested that possibly some of the sulfide underwent oxidation in contact with the air.

Determination of the Reaction Rate Constant

Using the work of Bullock and Forbes (4) as a basis, the reaction rate constant was determined, assuming that the rate determining reaction was one of second order. The following is the derivation of the formula used in calculating the second order reaction rate constant.

$$\frac{dx}{dt} = k\,(a - x)\,(b - x); \quad kdt = (a - x)\,(b - x)\,dx$$

where

a = initial concentration of 2 - nitrophenol - 4 - sulfonic acid

b = initial concentration of sodium sulfide

x = concentration of amine formed

Let $$\frac{1}{(a - x)\,(b - x)} = \frac{A}{a - x} + \frac{B}{b - x}$$

$$Ab - Ax + aB - Bx = 1$$

$$A + B = 0\ ;\ A = -B$$

$$Ab - aA = 1\ ;\ A = \frac{1}{b - a}\ ;\ B = \frac{1}{a - b}$$

$$kdt = \frac{1}{b - a}\left[\frac{dx}{a - x} - \frac{dx}{b - x}\right]$$

$$kt = \frac{1}{b - a}\left[-\frac{d\,(a - x)}{(a - x)} + \frac{d\,(b - x)}{(b - x)}\right]_0^x$$

$$kt = \frac{1}{b - a}\left[\ln\,(b - x) - \ln b - \ln\,(a - x) + \ln a\right]$$

$$k = \frac{2.303}{(b - a)t}\ \log\ \frac{a\,(b - x)}{b\,(a - x)}$$

Substituting values:

$a = 0.05$ mol/liter

$b = 0.08$ mol/liter

$x =$ calculated quantity of amine formed in mol/liter

$$k = \frac{2.3}{(.08 - .05)t} \quad \log \frac{.05\,(.08 - x)}{.08\,(.05 - x)}$$

$$k = \frac{76.77}{t} \quad \log \frac{1 - 12.5x}{1 - 20x}$$

The calculated results of the experimental work are shown in Table V.

TABLE V

CALCULATIONS FOR VELOCITY CONSTANTS OF SODIUM SULFIDE REDUCTION OF 2 - NITROPHENOL - 4 - SULFONIC ACID

SERIES I - 95° C.

t (min.)	x (mol/liter)	k (liter mol $^{-1}$ min. $^{-1}$)
4	0.0032	$19.2 \log \frac{1-0.040}{1-0.064} = 0.210$
10	0.0064	$7.68 \log \frac{1-0.080}{1-0.128} = 0.184$
20	0.016	$3.84 \log \frac{1-0.20}{1-0.32} = 0.269$
40	0.028	$1.92 \log \frac{1-0.35}{1-0.56} = 0.326$
60	0.032	$1.28 \log \frac{1-0.40}{1-0.64} = 0.284$
100	0.044	$0.768 \log \frac{1-0.55}{1-0.88} = 0.440$x
140	0.046	$0.547 \log \frac{1-0.575}{1-0.92} = 0.398$x
180	0.049	$0.425 \log \frac{1-0.612}{1-0.98} = 0.543$x
210	0.050	$0.365 \log \frac{1-0.625}{1-1.0}$

x = values not accepted

Average of accepted values = 0.255

TABLE V

SERIES II - 63° C.

t (min.)	x (mol/liter)	k (liter mol $^{-1}$ min. $^{-1}$)		
15	0.00092	5.11	$\log \frac{1-0.0115}{1-0.0184}$	$= 0.016$
80	0.0032	0.960	$\log \frac{1-0.040}{1-0.064}$	$= 0.0115$
835	0.0060	0.092	$\log \frac{1-0.075}{1-0.120}$	$= 0.002$
1345	0.0069	0.0570	$\log \frac{1-0.0863}{1-0.138}$	$= 0.0016$
2355	0.012	0.0326	$\log \frac{1-0.150}{1-0.240}$	$= 0.0016$
2750	0.013	0.0279	$\log \frac{1-0.163}{1-0.260}$	$= 0.0015$
3715	---	---	---	---

No average taken because of wide deviations.

CONCLUSION

A procedure adapted from the work of Bullock and Forbes (3) was used to determine the reaction velocity constants for the reduction of 2 - nitrophenol - 4 - sulfonic acid by sodium sulfide.

Two series of reductions were made. Series I was performed at a temperature of 95° C. while Series II was performed at 63° C. Following the work of Bullock and Forbes, (4), the overall reaction rate was assumed to be governed by a rate-determining reaction of the second order for various concentrations of the oxidizing and reducing agents.

Basing the calculations on the above assumption, fairly consistent values for the reaction velocity constant were obtained for Series I. The average of the consistent values taken was found to be 0.255 liter mol $^{-1}$ min. $^{-1}$.

Series II, however, showed wide deviations in the calculated values for the reaction velocity constant. Furthermore, the values for the reaction velocity constant drop sharply. It was observed that the quantity of sulfide ion appeared to diminish more rapidly than the formation of amine would indicate. Since the reduction of the nitro group was found to proceed very slowly at 63° C., it was necessary to increase the time interval for each individual reduction. It is suggested, that because of this additional exposure, appreciable quantities of sulfide ion were lost by air oxidation. This would account for the augmented consumption of sulfide ion and the sizeable drop in the values of the reaction velocity constants as the reaction time was increased.

REFERENCES

Bullock and Forbes, "Formation of Sodium Thiosulfate from Oxidation of Sodium Sulfides by Means of Aromatic Nitro Compound", *Journal American Chemical Society* Vol. 55, 1933, p.232.

Chemical Abstracts, (References to 2 - Aminophenol - 4 - Sulfonic Acid), *1950*, 5601c, 5601e, 6137g, 6138d, 6140e,6141f, 6144f, 6136f, 6648i, 7552i, 9681h, 10330d, 10335c; *1949*, 5964i, 8143i, 8147e, 8148e, 8150i, 8156f, 9466f, 3204i, 3625a, 4474i, 4482g, 4485g, 5194c, 5598h, 5600b, 5962b; *1948*, 767d, 3580f, 4759g, 7052f, 7053d; *1947*, 3070a, 1452b, d, 1455a; *1946*, 2634^{6}, 3904^{7}, 5421^{1}; *1944*, 6278^{4}; *1943*, 874^{2}; *1941*, 4157^{2}, 6671^{7}; *1939*, 6229^{4}; *1936*, 75545,^{9}; *1934*, 167^{1}, 4045^{5,6}.

Fiat Final Report No. 764, Dyestuff Manufacturing Processes of I. G. Farbenindustrie, A G, 18 April 1947, Dept. of Commerce, Office of Technical Services, PB 74026, p. 2297, PB 74025, p. 1690.

Fiat Final Report No. 1313, German Dyestuffs and Dyestuff Intermediates, 1 February 1948, Dept. of Commerce, Office of Technical Services, PB 85172, Vol. III, pp. 204, 205.

Fieser and Fieser, *Organic Chemistry*, 1st Edition, 1944, D. C. Heath and Company, Boston, Massachusetts, p. 863.

Fierz-David and Blangey, *Fundamental Processes of Dye Chemistry*, 5th Edition, 1949, Interscience Publishers, Inc., New York, N. Y. pp. 385, 386.

Groggins, *Unit Processes in Organic Chemistry*, 3rd Edition, 1947, McGraw Hill Book Co., New York, N. Y., pp. 77, 94, 95, 112.

Technical Manual and Year Book of American Association of Textile Chemists and Colorists, Vol. XXVIII, 1952, Howes Publishing Company, Inc., New York, New York, pp. 100 - 103.