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THE SYNTHESIS OF 2-AMINOPHENOL-4-SULFONIC ACID

BY

JOSEPH SALVATORE MILAZZO

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PART I

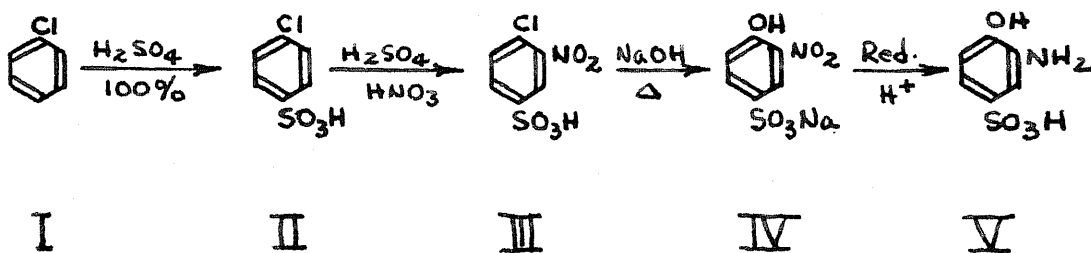
The Hydrolysis of Sodium 2 - Nitro - 1 - Chlorobenzene - 4 -
Sulfonate to Sodium 2 - Nitrophenol - 4 - Sulfonate

The Synthesis of 2 - Aminophenol - 4 - Sulfonic Acid

Introduction

A literature search showed that there are numerous methods of preparing 2 - aminophenol - 4 - sulfonic acid. It has been made by: reduction of 2 - nitrophenol - 4 - sulfonic acid (1,2); sulfonation of 2 - aminophenol (3); fusing aniline - 2,5 - disulfonic acid with sodium hydroxide (4); and nitrating phenol-p-sulfonic acid and reducing the product (5).

This investigation is concerned with the following synthesis as described in the BIOS report (2).



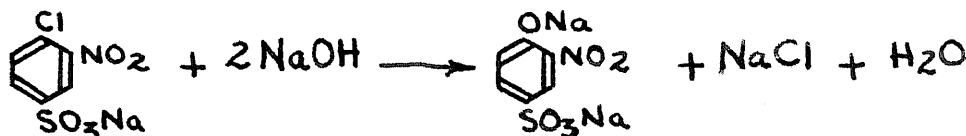
Not too much detailed information is available in the literature pertaining to the various compounds (6). This report deals mainly with an accurate study of the hydrolysis rate of sodium 2 - nitrochlorobenzene - 4 - sulfonate at various temperatures.

-
1. Post (Ann. 205, 52) (1880)
 2. British Intelligence Objective Sub-Committee 1946 (No. 1153)
 3. Levin J. 1882 1010, Vgl Groth Ch Kr 4, 337
 4. The Mfg. of Intermediate Products for Dyes J.C.Cain 2nd Edition 1919
 5. " " " " " " " " " " " " " " " "
 6. Ullmann 1932 Vol VIII, 351

The preparation of sodium 2 - nitrochlorobenzene - 4 - sulfonate proceeds in almost quantitative yield (96%) through the sulfonation and nitration of chlorobenzene, followed by its isolation by "liming" and its transformation to the sodium salt through the agency of sodium carbonate.

Before determining the hydrolysis rates of sodium 2 - nitrochlorobenzene - 4 - sulfonate at the various temperatures (61.2° C., 76.8° C., and 100° C.), and at known sodium hydroxide concentrations, a sufficient quantity of the intermediate mentioned above was prepared according to the BIOS report (2).

Since sodium chloride is formed during the hydrolysis,



it was possible to measure the reaction rate by the determination of the amount of this compound present at various intervals during the process, using the Volhard method. The experimental details follow.

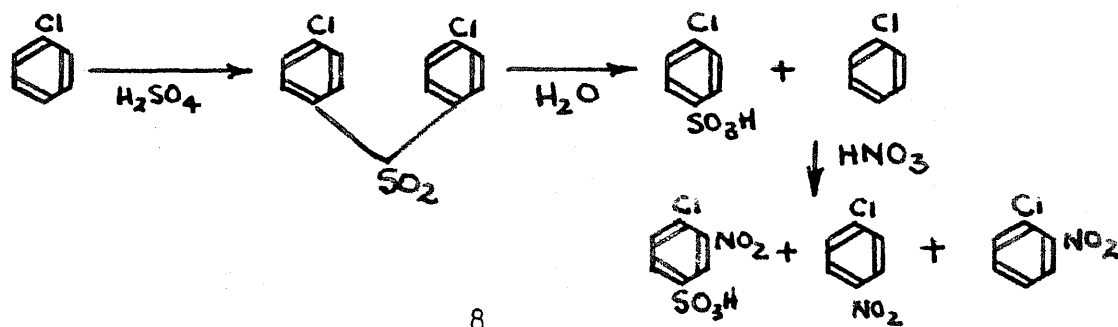
Experimental

Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate

In a half-liter 4-neck flask (ground glass) equipped with thermometer, stirrer, 125 ml dropping funnel and reflux condenser, there were placed 50 g. of chlorobenzene (0.444 moles). With agitation, in about 1/4 hr. there were added dropwise 187.5 g. of 100% sulfuric acid (1.913 moles). The temperature rose from 20° to 38° C. during the acid addition. The mixture was then heated to

95° - 100° C. and held for 2 hrs. At the end of this time no odor of chlorobenzene was noticeable and the mixture then was flesh color. It was cooled to 20° C. in an ice bath and in 1/2 - 1 hr. at 20° - 30° C. there was added dropwise 27.4 g. of 100% nitric acid (0.435 moles, 98% of theory). This was stirred at 24° - 25° C. for 6 hrs. (A slight excess of nitric acid was present and the amber-colored mixture was quite viscous). The viscous mixture was poured under stirring into a 4 liter beaker containing 1,276 g. of water at 20° - 25° C., 142 g. of lime (calcium hydroxide 1.918 moles), and 12.5 g. of sodium sulfate (0.0882 moles). The temperature rose to 75° C.(7). It was stirred until uniform (15 minutes), filtered on an 18.5 cm. Buechner funnel, and washed with hot water. The insoluble calcium sulfate cake was extracted with 1000 g. of water at 70° C. for 1/4 hr., filtered, and washed until the filtrate ran clear and colorless, indicating complete removal of the soluble yellow nitrosulfonate. The mother liquors and washes were collected in a weighed 4 liter beaker and the contents evaporated to about 200Be¹.

7. A sweetish odor detected after dilution was due to the presence of a byproduct, a mixture of ortho- and para nitrochlorobenzene which was probably formed by the hydrolysis and nitration of a small amount of p,p'-dichlorodiphenyl sulfone formed during the sulfonation:



Yield; 753 g. of liquor contained 110.69 g. sodium 2 - nitrochlorobenzene - 4 - sulfonate (96% of theory)(8). The compound was not isolated, but the hydrolyses were run directly on aliquot portions.

Hydrolysis Procedure

To a well-stirred solution containing 5.19 g. (0.02 mole) of sodium 2 - nitrochlorobenzene - 4 - sulfonate were added exactly 50 g. (0.05 mole) sodium hydroxide. The mixture was diluted with distilled water to exactly 200 ml. Precisely 20 ml. portions of the mixture were transferred by pipet to six different test tubes (25 mm x 200 mm). Each test tube was fitted with an air condenser made of pieces of glass tubing 24 inches long and 9 mm in diameter. The test tubes were placed at a given time in a 2-liter fusion pot which had a metal plate top containing seven holes, one for each of the test tubes and one for a condenser to enable refluxing of the various solvents in which the hydrolysis was to be run; (1) boiling water, 100° C., (2) boiling carbon tetrachloride, 76.8° C., and (3) boiling chloroform, 61.2° C. In each case, the temperature of the boiling solvent was checked with an accurate thermometer to insure the correct reading. The hydrolysis in each case was run a total of 5 hrs., but test tubes were removed from the boiling solvent after 1/2 hr., 1 hr., 2 hr., 3 hr., 4 hr., and finally at 5 hrs. A distinct color change was observed. It progressed during the hydrolysis from

8. Based on organic diazotization analysis of an aliquot. Siggia "Quantitative Organic Analysis via Functional Groups", John Wiley and Sons, New York, N.Y. 1949 p 70-72.

a yellow to a yellow orange and finally to a deep red orange. In order to make certain that the hydrolysis was stopped as soon as the test tubes were removed from the boiling solvents, the samples were cooled instantly with an ice bath and then the test tube contents were washed into a 500 ml. Erlenmeyer flask with 180 ml. distilled water. To the mixture was added about 2 ml. of nitric acid (1:1 by volume) to neutralize the excess sodium hydroxide and then a further 5 ml. (excess) of acid were added. A pale yellow clear solution resulted. Approximately 10 ml. of standard one-tenth silver nitrate were added and the mixture shaken until spongy flakes of silver chloride were obtained. Then, the mixture was cooled to 15° C. for the best end-point results and titrated with tenth normal ammonium thiocyanate after adding ferric alum indicator, which gave the sharp characteristic pale tan end-point of ferric thiocyanate. From these data it is possible to determine the rate of hydrolysis.

TABLE I

Analytical Data for the Hydrolysis of Sodium 2 - Nitro-
chlorobenzene - 4 - sulfonate at various temperatures

Experiment	Measured Time(min)	Adopted Time(min)	Volume in milliliters		
			AgNO ₃	NH ₄ CNS	(AgNO ₃ minus NH ₄ CNS)
#6 (100°C)	0	0	0	0	0
	30	0	10.01	6.26	3.75
	60	30	10.01	4.41	5.60
	120	90	15.00	6.75	8.25
	180	150	15.00	5.25	9.75
	240	210	15.00	4.14	10.86
	300	270	20.02	8.31	11.71
#7 (76.8°C)	0	0	0	0	0
	30	0	5.005	4.354	0.651
	60	30	5.005	3.904	1.101
	120	90	5.005	2.753	2.252
	180	150	10.01	6.75	3.26
	240	210	10.01	6.05	3.96
	300	270	10.01	5.45	4.56
#8 (61.2°C)	0	0	0	0	0
	30	0	5.005	4.700	0.305
	60	30	5.005	4.500	0.505
	120	90	5.005	4.350	0.655
	180	150	5.005	4.150	0.855
	240	210	5.005	4.050	0.955
	300	270	5.005	3.800	1.205

TABLE II

Hydrolysis Rates of Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate

Moles of Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate used	Concentration of Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate (molarity)	Hydrolyzing a) Agent (moles) b) % molar excess c) molar concentration	Hydrolysis T ^o C	Hydrolysis Time Minutes	% Chlorine Hydrolyzed
0.02 (Exp. #6)	0.10	a) NaOH (0.05)	100 ^o	30	18.73
		b) (25.0)		60	28.03
		c) (0.25)		120	41.27
				180	48.69
				240	54.24
			300	58.48	
0.02 (Exp. #7)	0.10	a) NaOH (0.05)	76.8 ^o	30	3.25
		b) (25.0)		60	5.49
		c) (0.25)		120	11.25
				180	16.23
				240	19.67
			300	22.72	
0.02 (Exp. #8)	0.10	a) NaOH (0.05)	61.2 ^o	30	1.52
		b) (25.0)		60	2.52
		c) (0.25)		120	3.27
				180	4.27
				240	4.78
			300	6.02	

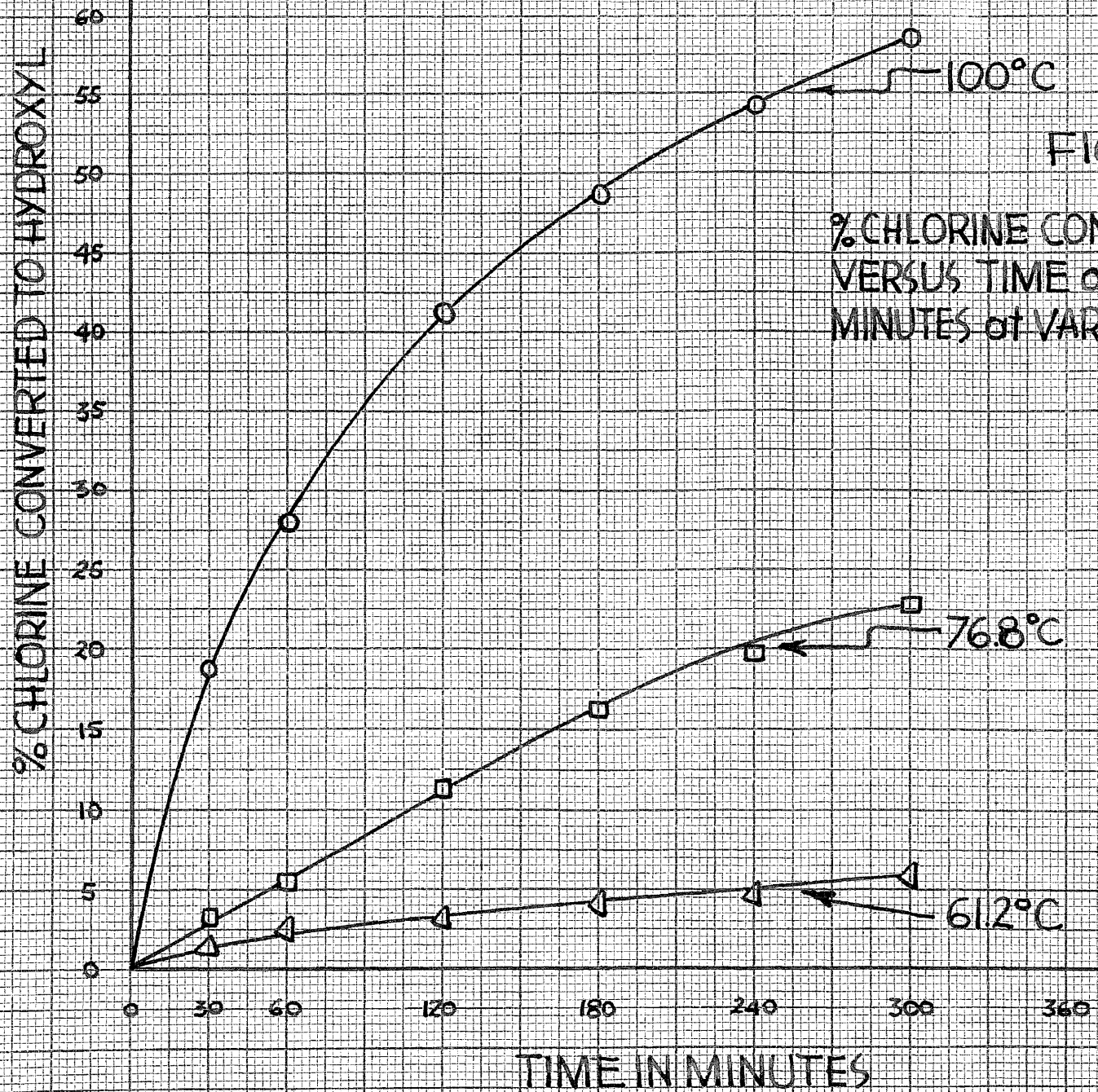


FIGURE I

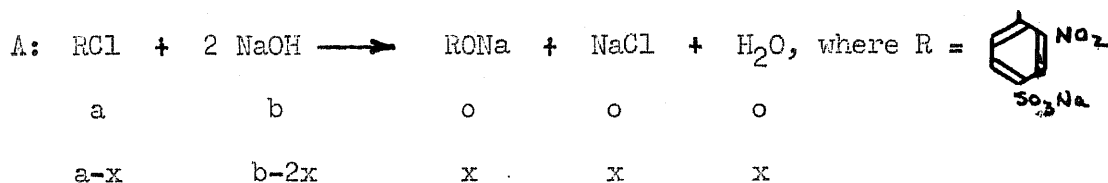
% CHLORINE CONVERTED TO HYDROXYL
VERSUS TIME OF REACTION IN
MINUTES AT VARIOUS TEMPERATURES

The hydrolysis rate curves of figure I page 13 reveal that under the conditions specified,

1. The greater the temperature the more chlorine hydrolyzed for a given time.
2. The rate curves follow a smooth curve rather than a straight line, indicating that the amount of chlorine hydrolyzed is not directly proportional to the length of time of the hydrolysis.

Derivation of the Velocity Equation

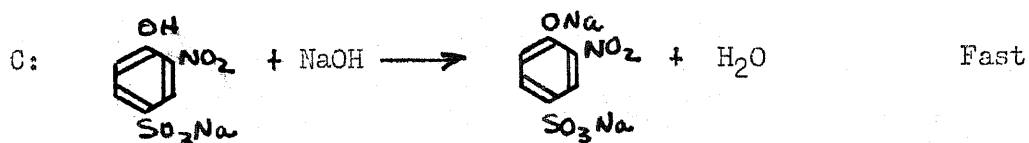
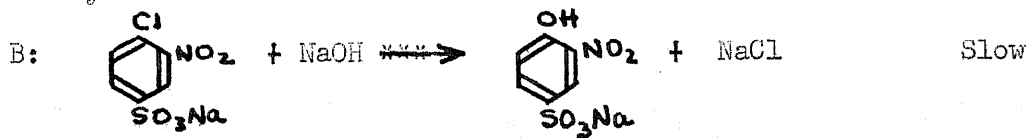
For the reaction of hydrolysis,



Let a and b represent the initial molarities of RCl and NaOH respectively; and at time, t, let x = molarity of the sodium chloride produced by the reaction.

Then, $\frac{dx}{dt} = K(a-x)(b-2x)$

Really two reactions are involved



It is assumed that A is the reaction which is actually measured.

Integration of $\frac{dx}{(a-x)(b-2x)} = Kdt$ by partial fractions

$$\int_0^x \frac{dx}{(a-x)(b-2x)} = \int_0^t Kdt$$

$$\frac{1}{(a-x)(b-2x)} = \frac{A}{(a-x)} + \frac{B}{(b-2x)} = \frac{Ab - 2Ax + aB - Bx}{(a-x)(b-2x)}$$

$$\text{Coefficients of } x, \quad -2A - B = 0 \quad B = -2A$$

$$Ab + aB = 1 \quad Ab - 2Aa = 1$$

$$A(b-2a) = 1$$

$$A = \frac{1}{b-2a}$$

$$B = \frac{-2}{b-2a}$$

$$Kt = \frac{1}{b-2a} \int_0^x \frac{dx}{a-x} - \frac{2}{b-2a} \int_0^x \frac{dx}{b-2x}$$

$$= -\frac{1}{b-2a} \int_0^x \frac{-dx}{a-x} + \frac{1}{b-2a} \int_0^x \frac{-2dx}{b-2x}$$

$$= -\frac{1}{b-2a} \int_0^x \frac{d(a-x)}{a-x} + \frac{1}{b-2a} \int_0^x \frac{d(b-2x)}{b-2x}$$

$$= -\frac{1}{b-2a} \left[\ln(a-x) \right]_0^x + \frac{1}{b-2a} \left[\ln(b-2x) \right]_0^x$$

$$= \frac{1}{b-2a} \left[\ln(b-2x) - \ln b - \ln(a-x) + \ln a \right]$$

$$= \frac{1}{b-2a} \left[\ln \frac{a}{b} \left(\frac{b-2x}{a-x} \right) \right]$$

$$\text{then, } K = \frac{2.303}{t(b-2a)} \log \frac{a}{b} \left(\frac{b-2x}{a-x} \right)$$

Since, we are measuring the rate of reaction taking our initial time 30 minutes after actual heating has begun (in order to make sure of a constant temperature throughout the measured period) we must take a and b as the concentrations of the chloro compound (III) and the sodium hydroxide at this adopted zero time.

The above equation can then be simplified somewhat by writing, $x = f a$, indicating f as the reacted fraction of a

$$\text{then, } K = \frac{2.303}{t(b-2a)} \log \frac{a}{b} \left(\frac{b-2fa}{a-fa} \right)$$

$$K = \frac{2.303}{t(b-2a)} \log \frac{1 - 2f \frac{a}{b}}{1 - f}$$

Example: Using figures from table II page 12 of the hydrolysis rates for temperature of 100° C.

$$a = 0.1(1 - 0.1873) = 0.08127 = 0.0813$$

$$b = 0.25 - 2 \times 0.01873 = 0.21254 = 0.2125$$

The equation now becomes,

$$\begin{aligned} K &= \frac{2.303}{t(0.2125 - 2(0.0813))} \log \frac{1 - 2f \frac{0.0813}{0.2125}}{1 - f} \\ &= \frac{2.303}{0.0499t} \log \frac{1 - 0.767f}{1 - f} \\ &= \frac{46.2}{t} \log \frac{1 - 0.767f}{1 - f} \end{aligned}$$

and the calculation of the velocity constant at 100° C. follows:

TABLE III

t	$1 - 0.767f$	$1 - f$	$\log \frac{1-0.767f}{1-f}$	$K = \frac{46.2}{t} \log \frac{1-0.767f}{1-f}$
30	0.9126	0.886	0.0129	0.020
90	0.788	0.722	0.0380	0.020
150	0.718	0.632	0.0554	0.017
210	0.665	0.563	0.0723	0.016
270	0.626	0.512	0.0873	0.015
Average K =				0.018

The value of ($K = 0.018$) velocity constant of the hydrolysis of sodium 2 - nitrochlorobenzene - 4 - sulfonate at 100°C . indicates that the assumption of a second order reaction (equation B page 14) was correct and that the stoichiometric equation A (of the third order apparently) actually represents the sum of a fast reaction (equation C) and a slow one (equation B).

The calculation of the velocity constants at 76.8°C . and 61.2°C . is given in Tables IV and V.

TABLE IV

t	$1 - 0.7946f$	$1 - f$	$\log \frac{1-0.7946f}{1-f}$	$K = \frac{46.0}{t} \log \frac{1-0.7946f}{1-f}$
30	0.9816	0.9768	0.00213	0.0033
90	0.9343	0.9173	0.00796	0.0041
150	0.8934	0.8658	0.01364	0.0042
210	0.8652	0.8303	0.01787	0.0039
270	0.8401	0.7988	0.02189	0.0037
Average K =				0.0038

TABLE V

t	$1 - 0.7974f$	$1 - f$	$\log \frac{1 - 0.7974f}{1 - f}$	$K = \frac{46.0}{t} \log \frac{1 - 0.7974f}{1 - f}$
30	0.9919	0.9898	0.00093	0.00140*
90	0.9858	0.9822	0.00160	0.00082
150	0.9778	0.9721	0.00256	0.00079
210	0.9736	0.9669	0.00299	0.00066
270	0.9636	0.9543	0.00428	0.00073
Average K =				0.00075

* - Because of its extreme deviation from the others, the first value has been rejected in the calculation of the average value of the constant for 61.2° C.

FIGURE II

LOG₁₀ K VERSUS 1/T

LOG₁₀ K

3.0

2.0

1.0

0

-1.0

-2.0

-3.0

Slope, taking points A and B:

$$\frac{y_A - y_B}{x_A - x_B} = \frac{-1.745 - (-3.050)}{0.00268 - 0.00301} = \frac{1.305}{-0.00033} = -3950$$

25.0

26.0

27.0

28.0

29.0

30.0

1/T X 10⁴

From the velocity constants at the three temperatures it is possible to calculate the activation energy of the hydrolysis. By transforming the Arrhenius Equation from its exponential form,

$$K = A e^{-\frac{\Delta E}{RT}}, \quad (1)$$

into its logarithmic form,

$$\log_{10} K = \log_{10} A - 0.4343 \frac{\Delta E}{R} \cdot \frac{1}{T},$$

it becomes evident that, in the latter form, the logarithm of the velocity constant, K, is a linear function of the reciprocal of the absolute temperature, and the slope of the line plotted from the data will be equal to

$$- 0.4343 \frac{\Delta E}{R}.$$

The slope when determined graphically (figure II) and equated to the above expression gives,

$$- 3950 = -0.4343 \frac{\Delta E}{R},$$

and from this it may be found that the value of ΔE (the energy of activation) is 18,100 cal. per mole.

- (1) where K = velocity constant for the reaction at temperature T°K
 A = constant (log₁₀ A is the y - intercept)
 e = base of natural logarithms, 2.718
 ΔE = Energy of activation
 R = gas constant
 T = absolute temperature of heating medium, °K.

PART II

Preparation of new Mono Azo Dyes Derived
from 2 - Aminophenol - 4 - Sulfonic Acid

A review of the literature shows that not many Azo dyes have been made from 2 - aminophenol - 4 - sulfonic acid. Cain (9), Shreve (10), and Schultz (11) have listed a few which are shown in Table VI.

TABLE VI

<u>Schultz Number</u>	<u>Name</u>	<u>Mf'g.</u>	<u>Other Intermediates Used</u>	<u>Dye Application Class</u>
	Acid Alizarin Brown B	B	m-phenylene diamine	mordant
231	Palatine Chrome Brown B	B		
232	Acid Alizarin Garnet	M	Resorcinol	mordant
	Acid Alazarin Violet N	M	B-naphthol	after chrome
233	Palatine Chrome Violet	B		
234	Diamond Black PV	By	1,5- dihydroxy naphthalene	mordant

B = Badische Anilin und SodaFabrik, Ludwigshafen

By = Farbenfabriken vorm F. Bayer E.P. 18569⁰², G.P.157786, U.S.P.722715

M = Farbwerke vorm Meister Lucius, Brüning, Höchst

The author has prepared certain new mono azo dyes by coupling 2 - aminophenol - 4 - sulfonic acid with R salt (disodium 2 - naphthol - 3,6 - disulfonate) and J acid (2 - amino - 5 - naphthol - 7 - sulfonic acid). These derivatives dye wool in very pleasing shades. After-chrome treatment of the dyed woolen fabrics causes the applied dyestuff to become very fast to light, washing, and soda treatment. An attempt was made to couple the acid (V) with Quinizarin (1,4 - dihydroxy anthraquinone) but this proved unsuccessful.

9. The Mfg. of Intermediate Products for Dyes (2nd Edition 1919) 129
J.C.Cain, MacMillan and Co.

10. Dyes Classified by Intermediates, R. Norris Shreve 1922.

11. Farbstofftabellen, G. Schultz, Akademische Verlagsgesellschaft
1931 Seventh Edition.

Experimental

I. The Coupling of 2 - Aminophenol - 4 - Sulfonic Acid with R Salt

Solution A

9.45 g. (0.05 mole) of 2 - aminophenol - 4 - sulfonic acid were placed in a 400 ml beaker containing 50 ml water at room temperature. To the mixture, with stirring, were added 3.5 g. (0.033 mole) soda ash. On stirring for 1/4 hr. complete solution with a light amber color resulted. Then 3.5 g. (0.051 mole) sodium nitrite were added and stirring was continued while cooling to 10° C.

Solution B

50 ml water were placed in a 400 ml beaker containing 15 ml (0.153 mole) concentrated hydrochloric acid. Solution A was then slowly run into solution B during a 15 minute period. The temperature was kept between 0° and 5° C. An amber color was developed, and a test with potassium iodide and starch showed free nitrous acid to be present.

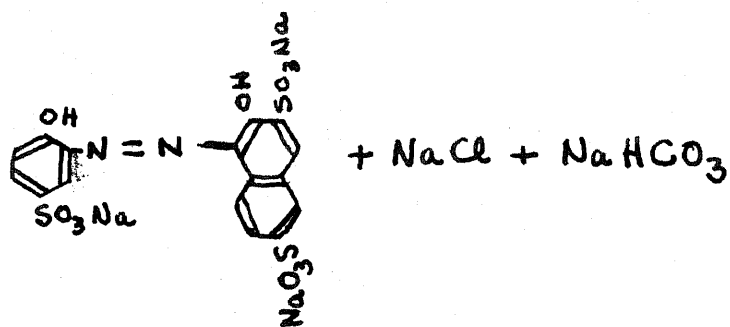
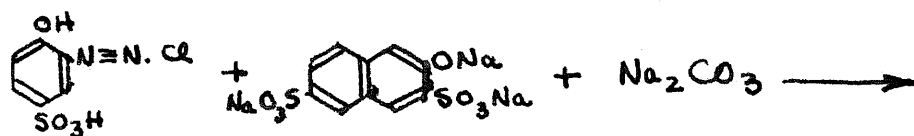
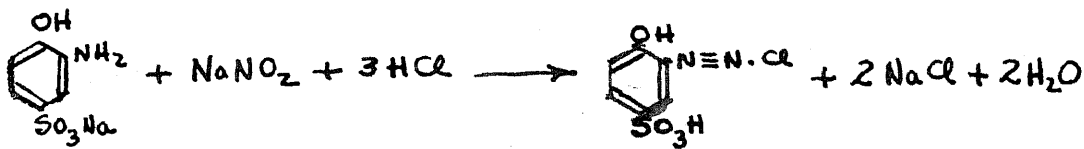
Solution C

17.4 g. (0.05 mole) of R salt (disodium 2 - naphthol - 3,6 - disulfonate) were placed in a 600 ml beaker containing 100 ml water at room temperature. With fast stirring there were added at 20° - 25° C. 11.2 g. (0.056 mole) sodium hydroxide and 12.5 g. (0.118 mole) soda ash. A yellow-brown solution with a greenish fluorescence was produced. The solution was

then cooled to 0° to 3° C. and to it was added with rapid agitation the mixture of A and B. This was done in about a half hour at a temperature below 8°C. A red-violet mixture resulted after stirring for an hour at 5° to 7° C. On heating between 90° and 100° C. for 15 minutes complete solution was obtained. The dissolved dye was separated from water solution by salting out with 75 g. (1.283 mole) sodium chloride and cooling the mixture to 25° - 30° C. in an ice bath. It was filtered on a 24 cm Buchner funnel, giving a dark violet, almost black, cake. It was dried as far as possible by suction and then completely dried in an oven at 80° - 90° C.

Yield: 43.0 g. 150% of Theory (considerable salt present).

The reaction may be expressed as follows:



This compound gives, with acid wool dyeing, a red orange shade, with after-chrome treatment, a maroon shade.



II. The Coupling of 2 - Aminophenol - 4 - Sulfonic Acid with J Acid

Solution A

5.2 g. (0.0275 mole) 2 - aminophenol - 4 - sulfonic acid were placed in a 400 ml beaker containing 27.5 ml water at room temperature. To the mixture were added with stirring 1.83 g. (0.0173 mole) of soda ash. This was stirred at 20° - 25° C. for a quarter of an hour. A light amber solution resulted. Then there were added 1.83 g. (0.0265 mole) of sodium nitrite. The mixture was stirred while cooling to 10° C.

Solution B

27.5 ml water were placed in a 400 ml beaker containing 8.3 ml (0.0844 mole) of concentrated hydrochloric acid at 0° C. Solution A was then run into Solution B, using the same technique as in Experiment I.

Solution C

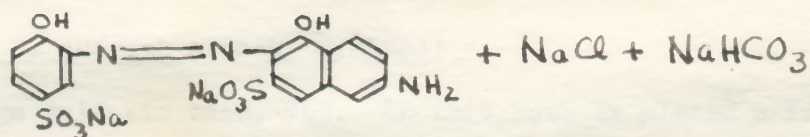
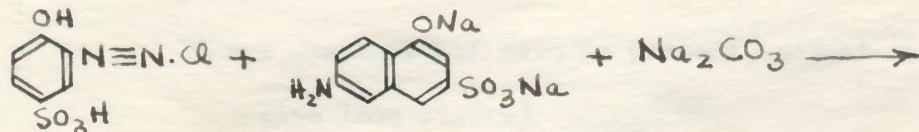
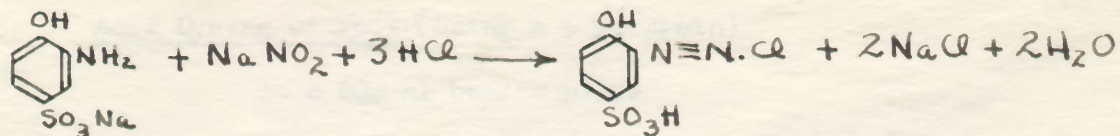
6.58 g. (0.0275 moles) J acid were placed in a 600 ml beaker containing 55 ml water at room temperature and to this there were added under vigorous stirring at room temperature 6.15 g. (0.0307 mole) of sodium hydroxide 6.9 g. (0.0651 mole) of soda ash

The dark amber solution which was formed was cooled to between 0° and 3° C. and Solution AB was carefully added in about one-half hour, keeping the temperature below 8° C. The mixture was stirred for an hour at about 5°C., and the resulting reddish orange solution was heated to 90° - 100° C. It became reddish violet. To it were added

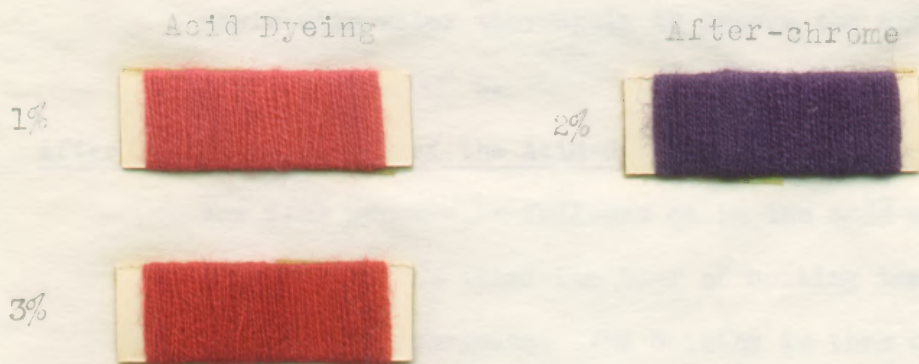
75 g. (1.283 mole) of sodium chloride. It was cooled to 20° - 25° C. and filtered on a 24 cm Buchner funnel. The black cake was sucked as dry as possible. It was finally dried in the oven at 80° - 90° C.

Yield: 40 g. (300% of Theory) considerable salt present.

The reaction may be expressed as follows:



With acid wool dyeing, an orange-brown shade is given. After-chrome treatment changes it a blue-black shade.



III. The Application of a Water-soluble Mono Azo Dye to Wool

Acid Dyeing of Wool (Using a 5 g. skein)

In a 600 ml beaker place

350 ml water

10 mgm dyestuff (if salt is present, adjust the weight to give this figure)

15 mgm sodium sulfate, anhydrous (used as a leveling agent to prevent streaky dyeings)

15 mgm sulfuric acid, 96%. In this bath is placed a five-gram woolen skein which has been wet in a 2% Igepon-T solution and then rinsed. The above mixture is raised to a boil and held for one hour.

Note: It is very important to turn the woolen skein repeatedly in the dye bath in order to get a level dyeing without any streaks. After one hour rinse the skein with water thoroughly to remove the excess dye. Then dry at 100° C.

After-Chrome Treatment of the Acid-dyed Wool

The same process is followed as in the acid dyeing of the wool except that after the hour of boiling there is added 5 mgm of sodium bichromate. The boiling is then continued for about three quarters of an hour. After this, the skein is removed, rinsed thoroughly, and dried at 100° C.

Note: The reason for after-chrome treatment of the acid-dyed wool is to obtain a fast dye which will hold up against light fading and washing. There may also be a change in shade and even in color.

PART III

The Preparation of Derivatives of Sodium 2 - Nitro - 1 -
Chlorobenzene - 4 - Sulfonate and Sodium 2 -
Nitrophenol - 4 - Sulfonate

A number of solid crystalline derivatives with definite melting points were prepared. The results are given in Table VII. Only one of these, the amide of 2 - nitrochlorobenzene - 4 - sulfonic, had previously been reported.

TABLE VII

Derivatives of Sodium 2 - Nitro - 1 - Chlorobenzene - 4 -

Sulfonate and Sodium 2 - Nitrophenol - 4 - Sulfonate

Name of Compound	Structural Formula	Molecular Weight	Molecular Formula	M.P. °C(1)	Neutral Equivalent Found (3)
p - toluidine salt of 2 - nitrochlorobenzene - 4 - sulfonic acid		344.5	$C_{13}H_{13}O_5ClN_2S$	232°-234°C. (dec)	341.3
aniline salt of 2 - nitrochlorobenzene - 4 - sulfonic acid		330.5	$C_{12}H_{11}O_5ClN_2S$	253°-254°C. (dec)	321.7
2 - nitrochlorobenzene - 4 - sulfonamide		236.5	$C_6H_5O_4ClN_2S$	175°-177°C.(2)	-
p - toluidine salt of 2 - nitrophenol - 4 - sulfonic acid		326.0	$C_{13}H_{14}O_6N_2S$	225°-228°C. (dec)	-

(1) All melting points were run with a calibrated thermometer.

(2) Agrees with literature (Intermediates for Dyestuffs. A. Davidson, 1926).

(3) See analytical section page 33.

Experimental

The p-Toluidine Salt of Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate(12).

5.35 g. (0.0296 mole) of sodium 2 - nitrochlorobenzene - 4 - sulfonate were dissolved in 16.1 ml of boiling water. To this solution was added 2.7 g. (0.0252 mole) of p-toluidine and 9.4 ml concentrated hydrochloric acid, C.P. The mixture was heated to boiling and held for five minutes (complete solution observed, and a dark amber color). The resultant solution was cooled, and the product crystallized out as yellow brown crystals. Filtered, and the product was recrystallized from a minimum amount of boiling water. A yield of 3.5 g. (49.3%) yellow crystals, m.p. 232°-234° C.(d). The composition was checked by determining its neutral equivalent. (see Table VII page 29).

The other aniline (12a) and toluidine (12b) salts were prepared using the same technique. (see Table VII page 29).

2 - Nitrochlorobenzene - 4 - Sulfonamide (13)

2 g. (0.0077 mole) sodium 2 - nitrochlorobenzene - 4 - sulfonate were placed in a 150 ml Erlenmeyer flask. To this was added
5 g. (0.024 mole) phosphorus pentachloride and the mixture was heated to 150° C. for one half hour (brown colored mixture resulted). Cooled to room temperature and 20 ml

12. "The Identification of Organic Compounds" Shriner and Fuson, John Wiley and Son, Inc., New York, N. Y. 1940 edition, p. 177
(a) ibid, (b) ibid

13. "The Identification of Organic Compounds" Shriner and Fuson, John Wiley and Son, Inc., New York, N. Y. 1940 edition, p. 176

benzene were added. Heated to boiling for a few minutes and filtered into 20 ml ammonium hydroxide (yellow crystals appear on the walls of the flask). Compound filtered and recrystallized from absolute alcohol. A Yield of 0.5 g. (27.5%) yellow prisms, m.p. 175° - 177° C. (see Table VII, page 29).

ANALYTICAL

I. Determination of the Purity of the Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate by Reduction and Titration with Standard Sodium Nitrite (8)(Diazotization Method).

4.473 g. of liquor were placed in a one liter beaker containing 200 ml distilled water at 20° - 25° C. and 50 ml concentrated hydrochloric acid, C.P. (very pale yellow clear solution was observed). At 20° - 25° C. were added 10 g. zinc dust (large excess was used to insure rapid reduction of the nitro compound). The above mixture was then heated to a gentle boil and held for about 5 - 10 minutes (unreacted zinc present, solution clear and colorless). Filtered on a 9 cm Buechner funnel which was filled with ice, rinsed the beaker with water and filtered; then, continued to wash the residue with about 100 ml distilled water to make certain that all of the reduced product was washed through. The filtrate and wash were then transferred to a one liter beaker, cooled to 5° - 10° C. and the clear solution titrated with 25.3 ml of one-tenth normal sodium nitrite to a blue-black end-point using potassium iodide and starch paper as an indicator.

The purity of the sodium 2 - nitrochlorobenzene - 4 - sulfonate is calculated from the formula:

$$\% \text{ purity based on diazotization} = \frac{\text{ml of nitrite} \times \text{normality} \times \text{milliequivalent wgt of compound} \times 100}{\text{weight of sample (gram)}}$$

II. Determination of the Chlorine Hydrolyzed in the Conversion of the Sodium 2 - Nitrochlorobenzene - 4 - Sulfonate to Sodium 2 - Nitrophenol - 4 - Sulfonate.

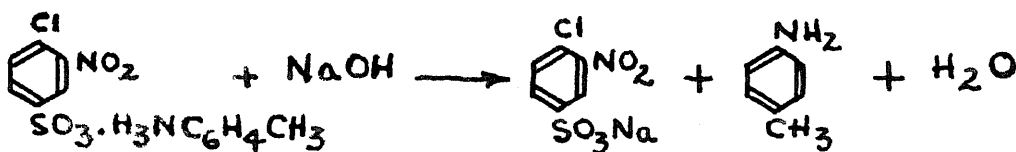
The Volhard method was used, titrating with ammonium thiocyanate and using ferric alum as the indicator (see experimental section page 10 where analytical procedure was included).

$$\% \text{ chlorine hydrolyzed} = \frac{\text{ml silver nitrate} \times \text{normality} \times \text{milliequivalent wt (chloride)} \times 100}{\text{weight of sample (gram)}}$$

III. Determination of the Neutral Equivalent of the Toluidine and Aniline Salt Derivatives by the Titration with Standard Sodium Hydroxide (14).

0.1 g. of the derivative weighed accurately were dissolved in about 100 ml absolute alcohol (complete solution resulted). The solution was then titrated with standardized tenth normal sodium hydroxide using phenolphthalein as an indicator. (The strong base would set free the weak base, toluidine or aniline, which does not affect the phenolphthalein).

Example: (p-toluidine salt of 2 - nitrochlorobenzene - 4 - sulfonic acid)



$$E = \frac{1000 \times W}{N \times V}; \quad \text{where } E = \text{Neutral Equivalent}$$

N = Normality of NaOH
V = Volume of NaOH (ml)
W = Weight of sample (gram)

14. "The Identification of Organic Compounds" Shriner and Fuson, John Wiley and Son, Inc., New York, N. Y. 1940 edition, p. 116

SUMMARY

The results of the hydrolysis of sodium 2 - nitrochlorobenzene - 4 - sulfonate indicate that a second order reaction was involved. Knowing the velocity constants at various temperatures it is possible to calculate the time of hydrolysis of the compound at any temperature when the molar concentrations of sodium hydroxide and sodium 2 - nitrochlorobenzene - 4 - sulfonate are known.

Monoazo dyes prepared during this investigation dyed wool in a weakly acid bath and even, deep, red-orange (page 24), orange-brown (page 26) shade and (after chrome treatment) a maroon (page 24), and a blue-black (page 26) shade. Solubility of the dyes were very good; the leveling and exhausting properties were excellent. Light fastness tests were performed in a fade-ometer (15) to determine the effect of ultra-violet light on the shade and color strength of the various dyes.

15. Atlas Color Fade-ometer Type FDA-R
Atlas Electric Devices Co., Chicago 10, Ill.