[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A STUDY OF THE MECHANISM OF THE PIRIA REACTION[1]

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The action of sodium bisulfite on *alpha*-nitronaphthalene leads to the formation of sodium naphthionate together with smaller amounts of the sodium salt of 1-amino-2,4-naphthalene disulfonic acid and *alpha*-naphthylamine. This type of transformation was first investigated by Piria, (1) and later by Hunter and Sprung (2) and by Lauer, Sprung, and Langkammerer (3).

The mechanism which was suggested involves, in the case of *alpha*-nitronaphthalene, the types of addition shown in Chart I.

It is apparent that the formation of one mole of *alpha*-naphthylamine gives three moles of sodium bisulfate while in the production of naphthionic acid two moles of sodium bisulfate result and in the case of *alpha*-naphthylamine-2,4-disulfonic acid only one mole of sodium bisulfate is produced.

The present study shows that the amount of sodium bisulfate actually corresponds to that predicted on the basis of this mechanism.

EXPERIMENTAL WORK

The Overall Standard Procedure of Hunter and Sprung (1) was used. A typical experiment follows:

A seven-gram sample (0.04 mole) of *alpha*-nitronaphthalene (m.p. 59–61°) was treated with twice the theoretical amount of sodium bisulfite (0.24 mole) in a total of 100 ml. of aqueous solution in a one-liter, round-bottom, three-necked flask equipped with a mercury-sealed mechanical stirrer and a reflux condenser. An absorption train containing dilute sodium hydroxide to absorb any sulfur dioxide evolved was connected to the top of the reflux condenser. The solution was refluxed for about five hours (until no odor of *alpha*-nitronaphthalene could be detected and the solution was homogeneous.)

The reaction mixture was then cooled and its volume was quickly determined. Portions of this solution were pipetted for the various sulfur determinations.

The volume of the remainder of the solution (about two-thirds) was measured and this was treated with 10 ml. of concentrated hydrochloric acid and boiled to expel the sulfur dioxide. The mixture was cooled, and the precipitated napthionic acid was removed by filtration. This crude material was added to 100 ml. of water, brought to a boil, cooled, and again filtered. This precipitate (naphthionic acid) was dried at 120°, weighed, and ground in a mortar for analysis.

The filtrate and the washings from the naphthionic acid were combined and evaporated to dryness. This product was weighed and ground in a mortar for analysis. It contained 2,4-disulfonic acid, *alpha*-naphthylamine hydrochloride, a trace of naphthionic acid, sodium chloride, and sodium sulfate. This material will be called the "disulfonic acid fraction".

The amounts of nitrogen in the naphthionic acid and in the disulfonic acid fraction were

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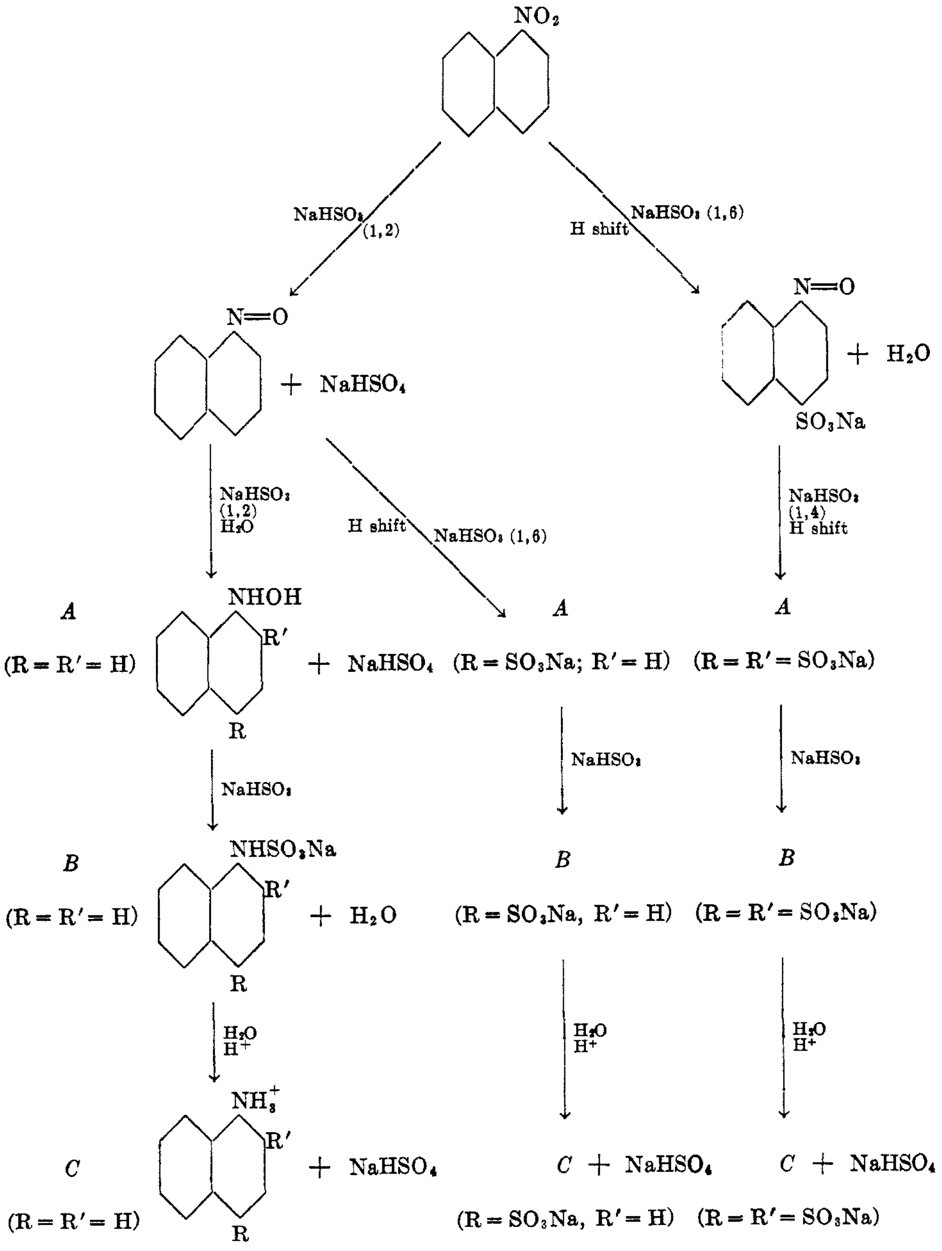
determined by the Kjeldahl-Arnold-Gunning method and expressed either as per cent purity of the substance under examination or as ml. of 0.1253 *N* alkali (N × 5.7).

CHART I



Sulfur balance. The sources of sulfate which are important in the present work are: (a) Sulfate in the original sodium bisulfite stock solution. (b) Sulfate formed in the reaction. (c) Sulfate from naphthionic acid. (d) Sulfate from the disulfonic acid fraction. They were determined as follows:

a. Sulfate in the original stock solution was determined by treating pipetted portions with concentrated hydrochloric acid, then boiling to remove all of the sulfur dioxide. Precipitation with barium chloride gave the original sulfate in terms of grams of barium sulfate per ml. of stock solution.

b. Sulfate formed in the reaction was determined by treating a pipetted portion of the reaction mixture with hydrochloric acid and boiling to remove all of sulfur dioxide. Precipitation with barium chloride as above gave the original sulfate plus the sulfate formed in the reaction. When the sulfate in the original sodium bisulfite stock solution is subtracted from the above total the difference (between b and a) is the sulfate formed in the reaction.

c. Sulfate equivalent to the naphthionic acid was calculated from the nitrogen as determined by the Kjeldahl-Arnold-Gunning method.

d. The sulfur in the disulfonic acid fraction was determined by precipitating the inorganic sulfate in a weighed portion. Another weighed sample was subjected to the action of Eschka mixture and heated. Treatment with bromine water and hydrochloric acid, followed by boiling to expel all excess bromine and carbon dioxide, was then followed by precipitation with barium chloride. The Eschka treatment gives the total sulfur, both organic and inorganic. Subtraction of the value for the inorganic sulfur leaves the organic sulfur.

When the nitrogen to organic sulfur ratios of the disulfonic acid fraction were determined, they were found to be over 0.5. This high ratio demonstrates that (excluding a very small amount of naphthionic acid present) there was some *alpha*-naphthylamine present. Consequently, the *alpha*-naphthylamine was removed by steam distillation from an alkaline solution of a weighed portion of the disulfonic acid fraction. After this treatment, nitrogen to organic sulfur ratios were very close to 0.5 which they should be if they represent only disulfonic acid.

CALCULATIONS

A method was devised for calculating the amount of *alpha*-naphthylamine and disulfonic acid in the disulfonic acid fraction without determining either of them. The method is based on the following known data:

1. The amount of pure naphthionic acid produced.
2. The total nitrogen in the disulfonic acid fraction.
3. The total sulfate formed in the reaction.

Let a = grams of naphthionic acid produced.
b = total grams of sulfate as barium sulfate.
c = total nitrogen in the disulfonic acid fraction expressed as ml. of 0.1253 *N* alkali (N × 5.7).
x = grams of *alpha*-naphthylamine in the disulfonic acid fraction.
y = grams of disulfonic acid in the disulfonic acid fraction.

Molecular weights used in the calculations are as follows:

Barium sulfate = 233; Naphthionic Acid = 223, Disulfonic acid monosodium salt = 325; *alpha*-Naphthylamine = 143.

The *nitrogen balance* will then be:

Nitrogen from *alpha*-naphthylamine plus nitrogen from disulfonic acid equals total nitrogen in the disulfonic acid fraction, or in symbols:

$$\frac{14x}{143} + \frac{14y}{325} = \frac{14 \times 0.1253c}{1000} \quad \text{(I)}$$

from which

$$2.2908\ x + y = 0.04105\ c \quad \text{(II)}$$

The *sulfur balance* will then be:

Sulfate from the formation of disulfonic acid plus the sulfate from the formation of *alpha*-naphthylamine = total sulfate formed minus the sulfate derived from naphthionic acid formation, or (in symbols):

$$\frac{233y}{325} + \frac{3 \times 233x}{143} = b - \frac{2 \times 233a}{223} \quad \text{(III)}$$

which gives

$$6.8662\,x + y = 1.40481b - 2.93533a \quad \text{(IV)}$$

Solving (II) and (IV) simultaneously gives

$$x = 0.307035b - 0.641543a - 0.00897202c \quad \text{(V)}$$

Once x is calculated from known data, then from equation (II),

$$y = 0.04105c - 2.2908x \quad \text{(VI)}$$

One of the assumptions on which these equations depend is that the only substances in the disulfonic acid fraction containing nitrogen are *alpha*-naphthylamine and disulfonic acid. However, some naphthionic acid might be present due to imperfect washing and in that case, its presence would be detected by a nitrogen to organic sulfur ratio over 0.5. The amount of naphthionic acid in the disulfonic acid can be calculated from the N to S ratio as follows:

Let n = weight fraction of naphthionic acid
1−n = weight fraction of disulfonic acid

then

$$\frac{\dfrac{n}{223} + \dfrac{1-n}{325}}{\dfrac{n}{223} + \dfrac{2(1-n)}{325}} = r = (N/S \text{ ratio}) \quad \text{(VII)}$$

Simplifying gives:

$$\frac{102n + 223}{446 - 121n} = r \quad \text{(VIII)}$$

As an example, in experiment 82, $r = 0.50207$, $n = 0.0056726$ and the weight of "disulfonic acid fraction" is 23.997, then 23.997 × 0.0056726 = 0.1361 grams of naphthionic acid in the disulfonic acid fraction. The sulfate in the disulfonic acid fraction = 12.4067 grams of barium sulfate. The sulfate due to disulfonic acid is

$$12.4067 - 0.1361 \times \frac{233}{223} = 12.2645 \text{ grams}$$

The ml. of 0.1253 *N* alkali which are equivalent to this amount of barium sulfate are

$$\frac{0.5 \times 12.2645 \times 1000}{233 \times 0.1253} = 210.04 \text{ ml.}$$

The ml. of 0.1253 *N* alkali equivalent to the naphthionic acid fraction are

$$\frac{0.1361 \times 1000}{223 \times 0.1253} = 4.87 \text{ ml.}$$

The total nitrogen from naphthionic acid and disulfonic acid in the disulfonic acid fraction is equivalent to 210.04 + 4.87 = 214.91 ml. However, the nitrogen by analysis from the disulfonic acid fraction is 259.89 ml. The nitrogen due to *alpha*-naphthylamine is equivalent to 259.89 − 214.91 = 44.9 ml.

TABLE I

	81	82	85	86
N/S ratio	0.47200	0.50207	0.56409	0.50381
n	0.0000	0.0056726	0.16789	0.010426
Naphthionic acid in disulfonic acid fraction, g	0.00	0.1360	4.266	0.3378
$BaSO_4$ due to naphthionic acid	0.00	0.1422	4.457	0.3530
0.1253 *N* alkali equiv. to naphthionic acid, ml	0.00	4.871	152.657	12.091
Total $BaSO_4$ in disulfonic acid fraction	11.9267	12.4067	9.9286	11.5677
Total *N* in disulfonic acid fraction	251.550	259.891	243.387	242.696
N in *alpha*-naphthylamine	47.312	44.975	0.000	38.539
Sulfate from disulfonic acid	5.963	6.132	2.736	5.607
Sulfate from *alpha*-naphthylamine	4.145	3.939	0.000	3.375
Sulfate from naphthionic acid	3.604	2.977	11.901	3.034
Total calculated sulfate	13.712	13.048	14.637	12.722
Total analytically determined sulfate	13.070	13.601	13.737	13.802
a	1.724	1.425	5.696	1.790
b	13.070	13.601	13.737	13.802
c	251.550	255.020	90.730	230.605
x	0.6501	0.9818	0.2504	1.020
y	8.8368	8.2194	4.2981	7.129
$BaSO_4$ in naphthionic acid. Disulfonic acid fraction	0.000	0.142	4.457	0.3530
$BaSO_4$ in disulfonic acid	12.671	11.785	6.163	10.222
Total $BaSO_4$ in disulfonic acid fraction calculated	12.671	11.927	10.620	10.575
Total $BaSO_4$ analytically determined	11.927	12.4067	9.929	11.568
Disulfonic acid fraction weight	24.375	23.997	25.406	32.403

TABLE II

SCHEDULED SUMMARY OF EXPERIMENTAL DATA

SERIAL NO.	SULFATE FORMED		SULFATE IN DISULFONIC ACID FRACTION	
	Calc'd	Exper. Deter.	Calc'd	Exper. Deter.
81	13.712	13.070	12.671	11.927
82	13.048	13.601	11.927	12.407
85	14.637	13.737	10.620	9.929
86	12.722	13.802	10.575	11.568
Average	13.505	13.553	11.448	11.458

The weight of *alpha*-naphthylamine is:

$$\frac{44.985 \times 0.1253 \times 143}{1000} = 0.8059 \text{ grams}$$

The following tabulation can now be made.
Sulfate as barium sulfate from disulfonic acid formation:

$$\frac{210.04 \times 0.1253 \times 233}{1000} = 6.132 \text{ grams}$$

Sulfate from naphthylamine formation:

$$\frac{44.98 \times 0.1253 \times 3 \times 233}{1000} = 3.939 \text{ grams}$$

Sulfate from naphthionic acid formation:

$$(1.390 \times 0.927 + 0.1361) \times \frac{2 \times 233}{223} = 2.977 \text{ grams}$$

(The naphthionic acid was 92.7% pure by analysis.)
The total 6.132 + 3.939 + 2.977 = 13.048 grams. Actually 13.601 grams of sulfate as barium sulfate was obtained by analysis.

Reversing the procedure and starting with the sulfate formed in the reaction, the naphthionic acid in the naphthionic acid fraction plus that in the disulfonic acid fraction, and the total nitrogen in the disulfonic acid fraction, we can calculate the amount of disulfonic acid. From this a check can be made on the amount of sulfate in the disulfonic acid fraction.

If we use the following values for a, b, and c
$a = (1.390 \times 0.927) + 0.1361 = 1.4251$, $b = 13.601$, and $c = 259.891 - 4.87 = 255.02$.
Then, $x = 0.9818$ grams of *alpha*-naphthylamine,
$y = 8.2194$ grams of disulfonic acid.
The sulfate in the disulfonic acid fraction is calculated from the naphthionic acid part and from the disulfonic acid.
Sulfate as barium sulfate in naphthionic acid:

$$0.136 \times \frac{233}{223} = 0.142 \text{ grams}$$

Sulfate in disulfonic acid: $8.2194 \times 2 \times \frac{233}{223} = 11.785$ grams
The total is 0.142 + 11.785 = 11.927 grams as compared to the analytical value of 12.4067 grams.

A summary of four experiments may be seen in Table I. Since all of these experiments began with the same amount of *alpha*-nitronaphthalene, it is reasonable to average these values (see Table II).

CONCLUSIONS

The above figures which show excellent agreement between the calculated values and the experimentally determined values of the sulfate formed in the reaction and the sulfate in the disulfonic acid fraction are in agreement with the views of Langkammerer and Lauer, and Hunter and Sprung.

The amount of sulfate formed in the reaction bears the relation to the various products that is predicted by this mechanism, and the calculations presented here show that when the proposed mechanism is assumed and the amount of sulfate formed in the reaction is taken as the basis of calculation, the amount of sulfur appearing as organic sulfur in the disulfonic acid fraction is in agreement with the analytical values.

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REFERENCES

(1) PIRIA, *Ann.*, **78**, 31 (1851).
(2) HUNTER AND SPRUNG, *J. Am. Chem. Soc.*, **53**, 1432, 1443 (1931).
(3) LAUER, SPRUNG, AND LANGKAMMERER, *J. Am. Chem. Soc.*, **58**, 225 (1936).