Identification of *p*-Aminobenzoic Acid Sulfate.—A sample was dissolved in the least possible *N* potassium hydroxide, and carefully acidified with 2 *N* hydrochloric acid. At the neutral point, a substance precipitated which was identified as *p*-aminobenzoic acid by mixed melting points. With bromine water it gave tribromoaniline and an ammonia soluble substance. The latter, after reprecipitation with acid, showed a decomposition range of 266–286°. (Reported by Sudborough for dibromo-*p*-aminobenzoic acid, 260–270°.)

Summary

1. A number of aromatic nitro compounds have been reduced with sodium bisulfite, and the solutions thus obtained have been boiled with mineral acids.

2. The quantities of amines and aminosulfonic acids which are produced in this manner have been determined.

3. Several other reduction products have been isolated and identified.

4. A standard procedure for studying the Piria reaction has been adopted, and comparable results thereby obtained.

5. Factors have been pointed out which affect the reaction and require further investigation.

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THE PIRIA REACTION. II. THE ROLE OF THE SULFAMINIC ACIDS[1,2]

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When the acid treatment which follows the reduction of a nitro compound in the "over-all" Piria reaction[3] is omitted, the principal product which can be isolated is a sulfaminic acid salt, of the general formula $RNHSO_3M$. The isolation of an N-sulfonated compound of this type was included among the original findings of Piria,[4] and thereafter similar products were mentioned by other early investigators.[5] However, that these sulfaminic salts were the *chief* products of the reaction when acid treatment was avoided was first emphasized by Weil,[6] who investigated a variety of aromatic nitro compounds, including alkyl nitrobenzenes,

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September 1928.

[2] Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[3] Hunter and Sprung, THIS JOURNAL, 53, 1432 (1931).

[4] Piria, *Ann.*, 78, 31 (1851).

[5] Hilkenkamp, *ibid.*, 95, 86 (1885); Smit, *Ber.*, 8, 1442 (1875).

[6] (a) Weil, German Patents 147,552 and 151,134, *Friedländer*, 7, 58, (b) 61 (1902); (c) Weil and Moser, *Ber.*, 55, 732 (1922); (d) Weil and Wassermann, *ibid.*, 55, 2533 (1922).

the alkyl esters of nitrocarboxylic acids, acylaminonitro compounds, nitrophenols, nitroamines and halogenated nitro compounds.

This consideration alone suggests a reasonable mechanism for the course of the "over-all" Piria reaction, which may be stated as follows: in the reduction stage, the nitro group is reduced to an amine or a sulfaminic acid or both; in the acid treatment stage, the sulfaminic acid is partly hydrolyzed to sulfuric acid and the same amine, and is partly rearranged to an aminosulfonic acid. In fact, it was this simple conception of the reaction which we set up as a working hypothesis at the start of our work. It is readily suggested by two considerations.

1. Many investigators have shown that the salts of sulfaminic acids are converted into aminosulfonic acids by baking, and in one or two cases the same is true of the free acid.[7]

2. Weil especially[6b] has pointed out that the addition of concentrated mineral acid aids the transformation of sulfaminic acids to the aminosulfonic acid derivatives. In more or less vague terms, other investigators have mentioned the same reaction.[8]

Against the hypothesis must be considered four opposed considerations.

1. The statement of certain investigators that "dilute" mineral acids hydrolyze the sulfaminic acids quantitatively,[9] though we were unable to find any who stated the concentration of acid used, or gave any quantitative data in support of this contention.

2. Weil himself, in another place,[6b] explicitly states that he does not believe that the sulfaminic acids are transformed into the aminosulfonic acids. He suggests that sulfonation may actually occur in the reduction stage, but offers no experimental evidence, nor any theoretical reason for his opinion.

3. Raschig[10] has suggested a mechanism of formation of sulfaminic acids and amino sulfonic acids, from a hypothetical common intermediate, an arylimino disulfonate, $ArN(SO_3Na)_2$.[11]

[7] Junghahn, *Ber.*, **35**, 3747 (1890); Seyewitz and Block, *Bull. soc. chem.*, [4] **1**, 320 (1907); Seyewitz and Noel, *ibid.*, [4] **3**, 497 (1908); Quilico, *Gazz. chim. ital.*, **56**, 620 (1926); De Ruijter de Wildt, *Rec. trav. chim.*, **23**, 173 (1904); Bamberger and Hindermann, *Ber.*, **30**, 654 (1897).

[8] We know of only one set of experiments concerning the effect of concentrated acids on sulfaminic acids which was both carefully performed and adequately reported, that of Bamberger and Kunze [*Ber.*, **30**, 2274 (1897)], who showed that potassium phenylsulfaminate, when treated with a few drops of concentrated sulfuric acid in glacial acetic acid and allowed to stand for eighty hours in the ice box, was converted to *o*-anilinesulfonic acid and that this, in turn, could be converted to sulfanilic acid by heating at 180–190° with concentrated sulfuric acid.

[9] See, for example, Traube, *Ber.*, **23**, 1653 (1890); *ibid.*, **24**, 360 (1891); Junghahn, *ibid.*, **31**, 1234 (1898).

[10] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Berlin, 1924, pp. 255–272.

[11] The isolation of a compound of this type has recently been reported by Engel

$$NaSO_3—Ar—NHSO_3Na \xleftarrow{\text{Rearr.}} ArN(SO_3Na)_2 \xrightarrow{\text{Hydrolysis}} ArNHSO_3Na$$

4. Disulfonic acids have been isolated at the end of the acid treatment stage,[12] and their presence is unaccounted for by any scheme ever suggested.

Viewing these conflicting ideas, it seemed that the first constructive step would be to ascertain, not whether sulfaminic acids could be rearranged, but whether they could be rearranged by acid of the concentrations ordinarily used in the acid treatment stage of the Piria reaction. Our own practice being to bring the reaction mixture to a concentration in the neighborhood of 2 *N* with respect to hydrochloric acid, it was decided to take representative sulfaminic acids and subject them to the action of a wide range of acid concentrations on each side of this point, in order to attain quantitative certainty on this single point. At the same time, it was planned that if two parallel reactions were actually found, kinetic studies would be carried out. The event showed, however, that over the range of concentration from about 0.5 to 5.35 *N*, only hydrolysis occurs. Though the opinion that the sulfaminic acids were not the precursors of the aminosulfonic acids has already been expressed, we believe that this is the first time that quantitative data of this type have been brought forward to settle the point.

Experimental Method

A definitely standardized procedure was employed. Several of the sodium salts of sulfaminic acids were prepared and purified. Weighed samples of these salts (contained in 50-cc. Erlenmeyer flasks) and measured volumes of a standardized hydrochloric acid were brought to temperature in a thermostat. Then the acid was added to the sulfaminate, the flask stoppered, and replaced in the thermostat until the reaction was complete.[13] The contents of the flask were then washed out into a beaker, heated to boiling and a boiling solution of barium chloride added. The precipitate of barium sulfate was filtered, washed, dried and weighed. The weight of sulfuric acid produced was calculated from the weight of the barium sulfate.

Materials

The sodium sulfaminates were prepared by the action of partially neutralized sodium bisulfite upon the corresponding nitro compounds, and [This Journal, **51**, 3483 (1929)] in a paper dealing with the cleavage of azo compounds by alkali sulfites.

[12] For example, Walter, German Patent 109,487, *Friedländer*, **5**, 70 (1899); Bucherer and Borsch, *J. prakt. Chem.*, [2] 111, 329 (1925); Meister, Lucius und Brüning, German Patent 92,082, *Friedländer*, **4**, 528 (1895); and numerous other patent citations.

[13] Preliminary runs, made to determine approximate speeds, indicated that with the most dilute acid used (*ca.* 0.5 *N*) the reactions were complete in about forty hours at 40°. The later runs were made in the neighborhood of 50°.

purified by repeated crystallization from water to which a few drops of alkali were added to prevent decomposition. In some cases it was impossible to free them entirely from admixed inorganic salts.

Sodium Phenyl Sulfaminate.—This is the most soluble of the salts used, and consequently was the most difficult to purify. After five recrystallizations from water, appreciable quantities of sodium chloride and sodium sulfate were still present. Therefore, to characterize the sulfaminate a small amount of the compound, further recrystallized until free from these salts, was dried for several days in a vacuum desiccator over calcium chloride. On analysis, it was found to contain one molecule of water of crystallization.

Anal. Calcd. for $C_6H_6NSO_3Na \cdot H_2O$: Na, 10.81. Found: Na, 10.85, 10.90.

The material which had been crystallized five times was then analyzed and found to contain 6.55% of sodium chloride, 4.78% of sodium sulfate and 13.99% of sodium, total. The composition of the sample was therefore as follows

Na_2SO_4, %	4.78, equiv. to	2.62% Na
NaCl, %	6.65, equiv. to	1.55% Na
$C_6H_6NSO_3Na \cdot H_2O$, %	88.58, equiv. to	9.57% Na
	Total	13.74% Na
	Found by analysis,	13.99% Na

Sodium *p*-Tolyl Sulfaminate.—The salt was purified by several recrystallizations from water and dried in a vacuum desiccator for seven days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, 11.01. Found: Na, 11.19, 11.28.

There was still a slight admixture of sodium sulfate, which caused the sodium analysis to be higher than the theoretical. A 0.4-g. sample gave 0.0071 g. of barium sulfate, equivalent to 0.0030 g. of sulfuric acid, or 1.08% of sodium sulfate.

Sodium *o*-Tolyl Sulfaminate.—A sample was crystallized from water until free from sodium sulfate. It was dried in a vacuum desiccator over calcium chloride for four days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, 10.13. Found: Na, 10.25.

Sodium *p*-Acetaminophenyl Sulfaminate.—The salt was crystallized from water until free from inorganic impurities and dried *in vacuo* over calcium chloride for sixty hours. It contained two molecules of water of crystallization.

Anal. Calcd. for $C_8H_9O_4N_2S \cdot 2H_2O$: Na, 8.00. Found: Na, 8.18, 8.15.

Results

The sodium sulfaminates were allowed to react with solutions of hydrochloric acid varying in concentration from 0.47 to 5.35 *N*. The results thus obtained are presented in tabular form.

Analytical Data on the Reaction between Sodium Sulfaminates and HCl[a]

Salt used	Runs	Sample, g.	Acid normality, max. and min.	H_2SO_4, calcd. for 100% hyd., g.
$C_6H_5NHSO_3Na \cdot H_2O$[b]	4	0.4	0.47–5.35	0.1755
p-$CH_3C_6H_4NHSO_3Na$[c]	3	.4	0.47–2.70	.1887
o-$CH_3C_6H_4NHSO_3Na$	3	.3	1.05–5.35	.1295
p-$CH_3CONHC_6H_4NHSO_3Na \cdot 2H_2O$	4	.4	1.07–5.35	.1362

H_2SO_4 found, g. (av.)	Av. dev. from mean, g.
0.1765	0.0021
.1894	.0022
.1287	.0029
.1346	.0004

[a] The reactions were carried out at temperatures between 47–50°, varying not more than ±1° during a given run. [b] The sample contained 4.78% of sodium sulfate, as mentioned above. The sulfate due to this admixture was, of course, considered in the calculations. [c] The sample contained 1.08% sodium sulfate. The correction was applied as before.

For all four of these salts the quantity of sulfuric acid produced was therefore, within analytical error, the amount which should have resulted from complete hydrolysis of the sulfaminate to the corresponding amine and sulfuric acid. This was true for all acid concentrations.

According to the standard procedure used in the study of the "over-all" Piria reaction,[3] the solutions were approximately 2 normal with respect to hydrochloric acid, after the addition of this reagent. Since the quantitative experiments covered a sufficiently wide range of concentrations on either side of this figure, we consider this to be definite proof that sulfaminic acids play no part in the production of nuclear sulfonated compounds during the Piria reaction.

The investigations are being continued in the attempt to discover the intermediate which does give rise to the sulfonated amines.

Conclusions

Several sodium salts of sulfaminic acids have been prepared and carefully purified, and their reactions with varying concentrations of hydrochloric acid studied. It has been shown that with acid concentrations from 0.5 to 5.35 normal, these sulfaminates hydrolyze quantitatively to sulfuric acid and the corresponding amines, giving absolutely no trace of aminosulfonic acids.

Hence the aminosulfonic acids which are produced by the "over-all" Piria reaction are certainly not formed by rearrangement of sulfaminic acids.

It is worthy of passing notice that this work affords one more instance of a suspected indirect substitution, which in fact does not occur.

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