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The Oximes and Imides of Benzenedisulphonic Acids.

By

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I. m-Benzenedisulphoxime.

By the action of nitrous acid upon m-benzenedisulphinic acid AUTENRIETH and HENNINGS (Ber., 35, 1399; 1902) obtained the corresponding oxime, to which they gave a cyclic constitution. In order to see whether this view of its constitution could be confirmed and, at the same time, to obtain further knowledge of the oxime, the following experiments were performed.

The disulphinic acid was prepared, according to C. PAULY's method (Ber., 9, 1595; 1876), by reducing m-benzenedisulphochloride with an excess of zinc dust in the presence of water at a slightly elevated temperature. After the reaction had taken place, a solution of sodium carbonate was added to the resulting mixture of zinc m-benzenedisulphinate, zinc oxychloride, unchanged zinc, and water, so as to change the zinc salts into the more soluble sodium salts. The filtered solution was concentrated on a water-bath, mixed with strong hydrochloric acid, and after removing the precipitated sodium chloride, if any, the strongly acid liquor was shaken with ether. The free acid then separated as a viscous liquid between the aqueous and the etherial layers.

The following procedure was also adopted and found to answer the purpose equally well. To the resulting mixture of zinc salts and unchanged zinc a slight excess of potassium carbonate was added, and the solution of the potassium salts so obtained was slowly evaporated in vacuo over sulphuric acid. Prismatic crystals of potassium m-benzenedisulphinate separated along with the crystals of potassium chloride. The latter often formed clusters of octahedra and could be easily mechanically separated from the prismatic crystals of the m-benzenedisulphinate. The yield is very small, as is also the case with the method above described, owing to the great solubility in water of both the free acid and the potassium salt.

To a mixed solution of an alkaline nitrite and m-benzenedisulphinate, dilute sulphuric or hydrochloric acid was added drop by drop with constant stirring, care being taken not to let the mixture become warm. A white voluminous precipitate of m-benzenedisulphoxime, consisting of fine short needles, was thrown down. This was washed with water and recrystallised from acetone or alcohol.

This substance is tolerably soluble in acetone or alcohol, slightly so in ether or acetic ether, insoluble in benzene, chloroform, carbon bisulphide and water; but the last solvent takes up a small quantity of it at higher temperatures and separates it as long needles on cooling. Crystallised from acetone the oxime forms hard colourless prisms, whilst from alcohol it crystallises in plates; both crystals contain the solvents which are partly given off on exposure to the air and completely driven away on heating at 100°. When boiled with alcohol for many hours the oxime is changed into a non-crystalline viscous substance. An aqueous solution of caustic soda or potash dissolves the oxime, which can

be reprecipitated by an acid. When the crystals of the oxime are heated in a capillary tube they begin to darken at 180°, become almost black at 210°, and decompose suddenly at 216° with evolution of a gas containing the oxides of nitrogen, and leaving a carbonaceous viscous residue of a strongly acid reaction. This temperature of decomposition is so sharply defined that it can be employed for the identification of the substance. The decomposition temperature is, however, very markedly lowered by the presence of even a small quantity of impurities.

The methods described above are not well suited for the preparation of the oxime on a large scale, as the yield of pure m-benzenedisulphinic acid is too small. The following procedure is found to give better results.

20 grammes of crystallised m-benzenedisulphochloride in powder are added in three or four portions to a flask containing 32 grammes of zinc dust, 20 c.c. of alcohol and 30 c.c. of water. Slight warming causes the reaction to begin. The addition of alcohol prevents the floating of the sulphochloride on the surface, this precaution being advantageous to the progress of the reaction. When the reaction is once started the temperature rises considerably, and care must be taken to maintain it at 50°–60°, the flask being shaken constantly during the process and any sulphochloride adhering to the neck of the flask being, from time to time, washed down into the flask with a fine jet of water. When all the sulphochloride has been added and a sensible heat evolution is no longer observed, the flask is warmed on a water-bath to complete the reaction and to boil off the greater part of the alcohol. While the flask is still kept warm on the water-bath a solution of sodium carbonate is added little by little until its contents acquire a faint alkaline reaction, so as to

ensure the complete precipitation of zinc carbonate. The solution is filtered, and the filtrate, together with the washings, is evaporated on a water-bath, in order to reduce the volume. After cooling it down to the ordinary temperature, or better to below 10°, 6 grammes of sodium nitrite are dissolved in it, and then dilute sulphuric acid is added in small quantities with constant stirring, the solution being kept continually cooled so as to avoid the rise of temperature. At first the solution acquires a red tint,[1] which, however, fades away on the continued addition of the acid, and then a white crystalline precipitate of m-benzenedisulphoxime begins to appear. After adding an excess of dilute sulphuric acid the precipitated oxime is set aside for some time, which is then collected upon a filter, washed with water, and dried in a desiccator over sulphuric acid. When the operation is well conducted the dried mass amounts to over 15 grammes, or about 90% of the theoretical yield. The crude oxime is recrystallised from hot acetone, which is the best solvent for it. The solubility of the oxime in boiling acetone is about 5 parts in 100; but the solution can attain a considerable degree of supersaturation and furnishes well formed crystals on evaporation or cooling. The decomposition point of the pure crystals is exactly 216°.

Analytical data.

a) 0.2237 gr. of the crystals from the alcoholic solution, on drying at 100°, lost 0.0286 gr.

	Found	Cal. for $\{C_6H_4(SO_2)_2NOH\}_2 \cdot 1\frac{1}{2}C_2H_6O$
Alcohol	12.78%	12.79%

1. The coloration seems to be due to some impurity, because on repeating the same reaction with a salt of pure m-benzenedisulphinic acid no coloration was observed.

b) 0.2616 gr. of the crystals from the solution in acetone, on drying at 100°, lost 0.0199 gr.

	Found	Cal. for $\{C_6H_4(SO_2)_2NOH\}_2 \cdot \frac{1}{3}C_3H_6O$
Acetone	7.61%	7.60%

Estimations of nitrogen and sulphur were made with the crystals containing acetone.

c) Nitrogen.

0.1374 gr. gave 6.8 c.c. of moist nitrogen at 25°, 751 m.m.
0.1604 „ „ 8.0 „ „ „ „ „ 23°, 756 „

Nitrogen found	5.56%
	5.51 „
„ calculated	5.52 „

d) Sulphur.

0.1199 gr. gave 0.2214 gr. of barium sulphate.

Sulphur found	25.36%
„ calculated	25.19 „

e) Molecular weight.

It seldom happens that a divalent radical closes itself upon the meta-positions. This led me to suspect that the group NOH must be connected with two SO_2 groups of different benzene rings and that, consequently, the oxime must have a double formula. In order to decide this point the molecular weight of the oxime was determined by observing the elevation of the boiling point of acetone solutions.

Molecular weight found	452, 477, 485
Calculated for $HON\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2\\SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix}NOH$	470

The results are in good agreement with the foregoing supposition and make AUTENRIETH and HENNING's view of the cyclic constitution of this compound doubtful.

The oxime strongly resists the action of bromine, and sulphuric and hydrochloric acids, concentrated as well as dilute. No hydroxylamine is obtained on heating the substance with dilute hydrochloric acid to 140° in a sealed tube. Zinc dust and caustic soda reduce the oxime and give ammonia and m-benzenedisulphinic acid. Sulphur dioxide reduces it to the corresponding imide with a good yield. The action of fuming nitric acid is also a reducing one, the imide being formed; but the greater portion of the substance seems to be decomposed by it, and a notable quantity of sulphuric acid can be detected among the products of decomposition. The last two reactions will be specially described in the sequel.

II. m-Benzenedisulphimide.

This compound may be prepared by reducing the corresponding oxime in an alcoholic solution in the same manner as in the case of the monosulphonic acid (see Art. 13 of this volume).

For this purpose 5 grammes of the crude oxime were placed in a flask, covered with 20 c.c. of alcohol, and a small quantity of water was added to it. A current of sulphur dioxide was passed into this mixture to saturation, the temperature being kept, at first, at about 50°, afterwards at 60° or a little higher, until all the oxime had gone into the solution. The completion of the reaction was ascertained by taking out a small portion

of the solution and adding water to it, and seeing whether it gave any precipitate or not. When the reduction was complete, air was passed through the mixture to remove the excess of sulphur dioxide; and then some water was added. On neutralising the solution with potassium carbonate, voluminous crystals of the potassium salt of the imide filled the liquid, which, however, dissolved again on warming. The solution was concentrated on a water-bath, and set aside to crystallise. 3.25 grammes of the pure potassium salt, crystallised in needles, were thus obtained. In order to get the free imide, an excess of a solution of mercurous nitrate was added to the warm solution of the potassium salt, when the mercurous salt appeared as a white crystalline precipitate. This precipitate was washed, suspended in water, and decomposed by a current of hydrogen sulphide. The precipitated sulphide was filtered off, and the solution was evaporated on a water-bath until it became somewhat syrupy. On setting it aside for a while, the solution gave prismatic crystals of the imide, containing two molecules of water of crystallisation. The water of crystallisation can be removed at 100°.

When a considerable quantity of the imide is to be prepared, the conversion of the potassium salt into the mercurous salt, with the subsequent removal of mercury by means of hydrogen sulphide becomes a very tedious operation. It is better to evaporate the reduced alcoholic solution at once with the addition of a little water, until the crystals begin to appear. In this way a crop of tolerably pure imide can be obtained. The mother liquors from the recrystallisation can be worked up for various salts of the imide, or the free imide may be obtained through the mercurous salt as described above.

The free imide, which is very soluble in water, as well as in alcohol, has a strong acid reaction. It can be precipitated from the aqueous solution by adding strong sulphuric or hydrochloric acid. Even a very dilute solution of the imide gives a crystalline precipitate on the addition of an equal volume of strong hydrochloric acid. The imide has a bitterish sour taste. The ammonium salt is tolerably soluble in water and readily crystallises in short prisms. The potassium salt is also somewhat soluble in water and crystallises in long needles of a pearly lustre.

The most remarkable property of this imide is the slight solubility of the sodium salt, the solution saturated at 24° being about 0.04 normal. It can, therefore, be employed for the detection of sodium. The sodium salt is, however, tolerably soluble in hot water, from which it can be obtained in flat plates. The salts of barium and lead form prismatic crystals of less solubility. The silver salt is also slightly soluble and crystallises in white needles. It can be obtained by adding a solution of the free imide to a solution of silver nitrate. A double salt of silver and potassium was obtained as a white crystalline precipitate by adding silver nitrate to a warm solution of the potassium salt. The mercurous salt forms an insoluble white heavy crystalline precipitate.

Analytical data.

m-Benzenedisulphimide.

a) Water of crystallisation.

0.1217 gr., on drying at 100°–105°, lost 0.0093 gr.

Water found 7.64%

Calculated for $HN\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2\\SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix} NH,\ 2\,H_2O$ 7.60 „

b) Sulphur and nitrogen were estimated with the anhydrous substance.

0.1124 gr. gave 0.2420 gr. of barium sulphate.

Sulphur found 29.56%
„ calculated 29.25 „

0.1688 gr. gave 9.3 c.c. moist nitrogen at 11.5° and 750 m.m.

Nitrogen found 6.45%
„ calculated 6.40 „

The potassium salt.

a) Water of crystallisation.

0.1403 gr., on heating to 200°, lost 0.0071 gr.

Water found 5.06%

Calculated for $KN\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2\\SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix} NK,\ 1\tfrac{1}{2}\,H_2O$ 4.99 „

b) Potassium, determined as sulphate by heating the salt with sulphuric acid and igniting.

0.1403 gr. gave 0.0453 gr. potassium sulphate
0.2026 gr. „ 0.0653 gr. „ „

Potassium found 14.50%
14.47 „
„ calculated 14.45 „

c) Solubility.

1.6293 gr. of the aqueous solution saturated at 24° gave 0.0250 gr. of potassium sulphate on evaporation and ignition with sulphuric acid.

Hence 100 parts of the solution contain 4.76 parts of the anhydrous salt.

The sodium salt.

a) Water of crystallisation.

0.1358 gr., on drying at 100°–105°, lost 0.0240 gr.

Water found	18.11%
Calculated for $NaN\begin{Bmatrix}SO_2\cdot C_6H_4\cdot SO_2\\SO_2\cdot C_6H_4\cdot SO_2\end{Bmatrix}NNa,\ 6H_2O$	18.31 ,,

b) Sodium.

0.1358 gr. gave, on ignition with sulphuric acid, 0.0322 gr. sodium sulphate.

0.1678 gr. gave 0.0404 gr. sodium sulphate.

Sodium found	7.69%
	7.81 ,,
,, calculated	7.81 ,,

c) Solubility.

1.9852 gr. of the aqueous solution saturated at 24° gave 0.0057 gr. of sodium sulphate.

Hence 100 parts of the solution contain 0.97 parts of the anhydrous salt.

The silver salt.

This salt contains no water of crystallisation.

0.2787 gr. gave, on ignition, 0.0924 gr. metallic silver.

Silver found	33.16%
Calculated for $AgN\begin{Bmatrix}SO_2\cdot C_6H_4\cdot SO_2\\SO_2\cdot C_6H_4\cdot SO_2\end{Bmatrix}NAg$	33.10 ,,

The double salt of silver and potassium.

0.1943 gr. gave, on boiling with dilute hydrochloric acid, 0.0463 gr. silver chloride.

0.2127 gr. gave 0.0496 gr. silver chloride.

Silver found	$\begin{cases}17.94\% \\ 17.56\ ,,\end{cases}$
Calculated for $AgN\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix}NK$	18.52 ,,

III. p-Benzenedisulphoxime and the Imide.

These compounds can be prepared from p-benzenedisulphochloride in the same manner as that already described for the meta-isomer, pure p-benzenedisulphochloride being obtained as a by-product in the preparation of benzenetrisulphochloride according to the method of JACKSON and WING (Amer. Ch. Journ., 9, 332; 1889). The disulphochloride obtained in this way seems to be the purest ever prepared, there being no need of purifying it from the meta- and ortho-isomers. The disulphochloride was repeatedly crystallised from ether, until its melting point was found to be 140.5°.

p-Benzenedisulphoxime.

The reduction of p-benzenedisulphochloride by zinc dust took place as easily as in the case of the meta-compound, and gave the sparingly soluble zinc salt of the corresponding sulphinic acid. This was converted into an alkaline salt, and treated with sodium nitrite and dilute sulphuric acid. The oxime of p-benzenedisulphonic acid was obtained as a very fine white pre-

cipitate, difficut to filter and wash without loss. The yield was about 60% of the theoretical amount.

This oxime is slightly soluble in alcohol and acetone, and almost insoluble in other ordinary solvents. Acetone is the only solvent that can be employed for the purpose of recrystallisation. From this menstruum the oxime crystallises out on evaporation in thin plates, the crystals retaining a part of the solvent, which can be driven off on heating to 100°. There is practically no loss on recrystallisation. On heating this compound in a capillary tube it decomposes suddenly at 210° in the same manner as the meta-oxime, and the temperature can be used for the purpose of identification. Like the latter it changes into a viscous substance when boiled with alcohol, and, indeed, so quickly that crystals are hardly obtainable from an alcoholic solution. The oxime dissolves easily in caustic alkalies, and is reprecipitated on acidulation. The reactions with zinc and caustic soda, ammonia, and nitric acid are almost analogous to those of the meta-compound.

It is possible and even likely that this oxime has also a double molecular formula, but the molecular weight determination was not attempted on account of its slight solubitity in acetone.

Analytical data.

a) Acetone of crystallisation.

0.1398 gr., on drying at 100°, lost 0.0221 gr.

Acetone found	15.81%
Calculated for $HON\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2\\SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix}NOH,\ 1\frac{1}{2}\ C_3H_6O$	15.61 „

b) Nitrogen.

0.1373 gr. of the crystals gave 6.0 c.c. moist nitrogen at 15° and 754 m.m.

Nitrogen found	5.04%
„ calculated	5.04 „

c) Sulphur.

0.1245 gr. of the crystals gave 0.2075 gr. of barium sulphate.

Sulphur found	22.90%
„ calculated	23.01 „

p-Benzenedisulphimide.

This imide was obtained by reducing the oxime by means of sulphur dioxide. The powdered oxime was suspended in aqueous alcohol contained in a flask, sulphur dioxide passed to saturation, and the whole kept at a temperature of about 50°. Complete dissolution did not take place even when the reduction was complete, owing to the slight solubility of the imide in alcohol and consequent precipitation of it as the oxime was dissolved and reduced. Three or four hours were necessary before complete reduction took place, which could be ascertained by adding a drop of the reacting mixture into water, when complete disappearance of the turbidity was observed. The small solubility of the imide in water and especially in alcohol made the purification of this substance very easy. The contents of the flask were transfered into a dish and evaporated over a water-bath to a small bulk. The mother liquor was pressed out of the crude crystals of the imide which separated out on cooling, and the latter washed with a small quantity of alcohol.[1] Recrystallisation from water yielded the pure product.

1. From 2.3 gr. of the oxime 1.6 gr. of the crude imide were obtained.

p-Benzenedisulphimide crystallises in colourless prisms, with two molecules of water, which can be driven off at 100°. This imide behaves much like the corresponding meta-compound and can be precipitated from its aqueous solution by strong acids. The alkaline salts of the imide are sparingly soluble in water, even hot water not taking up much of them. Under the microscope they present the appearance of rhombic plates. Silver and mercurous salts form white, heavy, crystalline precipitates. The free imide has a sour taste, not accompanied, however, by any bitterness like that of the meta-compound. The small quantity of pure p-benzenedisulphochloride at my disporal made any further examination of these salts impossible.

Analytical data.

p-Benzenedisulphimide.

a) Water of crystallisation.

0.1220 gr., on drying at 100°–105°, lost 0.0092 gr.

Water found	7.54%
Calculated for $HN\begin{Bmatrix}SO_2 \cdot C_6H_4 \cdot SO_2\\SO_2 \cdot C_6H_4 \cdot SO_2\end{Bmatrix} NH,\ 6\ H_2O$	7.60 ,,

b) Sulphur.

0.1128 gr. of the anhydrous imide gave 0.2440 gr. of barium sulphate.

Sulphur found	29.72%
,, calculated	29.25 ,,

c) Nitrogen.

0.1861 gr. of the anhydrous imide gave 9.9 c.c. of moist nitrogen at 13° and 767 m.m.

Nitrogen found	6.30%
,, calculated	6.40 ,,

IV. Oximes and Imides of o-Benzenedisulphonic Acid.

The difficulty of procuring the materials was strongly felt in the investigation of the oxime and the imide of o-benzenedisulphonic acid. The starting point was p-bromaniline-o-sulphonic acid, and this was transformed into p-brom-o-benzenedisulphonic acid according to the method of ARMSTRONG and NAPPER (Chem. News, **82**, 46; 1900). Only two grammes of p-brom-o-benzenedisulphochloride was at my disposal, from which I had to prepare the oxime and also the imide.

A small quantity of potassium p-brom-o-benzenedisulphonate was debrominated with zinc dust and caustic potash, and from the product o-benzenedisulphochloride was prepared. But the quantity under manipulation was less than one gramme.

From these sulphochlorides the corresponding oximes and imides were prepared according to the methods already described but owing to the small quantity of the materials it was difficult to make many analyses.

The *oxime of p-brom-o-benzenedisulphonic acid* is tolerably soluble in acetone and alcohol, and crystallises from the former solvent in well defined prisms. Sulphur was estimated in the sample dried at 100°–150°, with the following result:

0.1374 gr. gave 0.2076 gr. of barium sulphate.

Sulphur found	20.75%
Calculated for $HON:(SO_2)_2C_6H_3Br$	20.38 „

In order to see whether this ortho-compound has the cyclic monomolecular constitution or not, its molecular weight was determined by observing the elevation of the boiling point of acetone. The result agreed exactly with the monomolecular formula.

The oxime decomposes on heating with an evolution of gas bubbles, but without charring; the decomposition point is 82°. On reducing it with sulphur dioxide a crystallisable acidic imide was obtained, which gave sparingly soluble alkaline salts. But no analysis was attempted.

The *oxime of o-benzenedisulphonic acid* was obtained in colourless prismatic crystals from its solution in acetone. Its decomposition point was very low and found to be about 45°. It was, therefore, impossible to recrystallise this compound from boiling acetone. On reduction it gave an acidic imide, but the substance was not analysed.

Both oximes are insoluble in water. They are readily decomposed by ammonia, with a brisk evolution of gas bubbles.

It can not be doubted that o-benzenedisulphonic acid gives the corresponding oxime and imide, but as no analyses were made it will be necessary to renew the investigation with larger quantities of the materials.

V. Action of Ammonia and Fuming Nitric Acid upon the Oximes.

Aqueous ammonia acts violently upon the sulphoximes described above with evolution of nitrogen and formation of the corresponding sulphinic acids, while a good deal of heat is liberated during the reaction. Evolution of nitrogen by the action of ammonia upon benzenesulphohydroxylamine $C_6H_5 \cdot SO_2 \cdot HNOH$ was observed by PILOTY (Ber., 29, 1559; 1896), but without any special study of that reaction. The action of ammonia upon m-benzenedisulphoxime may be considered to be a typical reaction of an aromatic sulphoxime, and may be formulated as follows:

$$\left.\begin{matrix} -SO_2 \\ -SO_2 \end{matrix}\right\rangle NOH + NH_3 = \begin{matrix} -SO_2H \\ -SO_2H \end{matrix} + N_2 + H_2O,$$

the group SO_2 being directly attached to the benzene ring. In order to ascertain to what extent this reaction takes place, the nitrogen gas liberated by the action of ammonia upon m-benzenedisulphoxime was measured in the following manner.

0.1387 gr. of m-benzenedisulphoxime crystals containing acetone was put into a small thin glass bulb, which was evacuated by means of a water-pump and then sealed. This bulb was introduced into a wider tube of about 100 c.c. capacity, the lower end of which had been drawn out and sealed. The upper end of the tube was then drawn out to a capillary, through which moderately strong ammonia water was introduced, until about one third of the tube was filled, and the capillary connected with the water pump in order to evacuate the tube. The ammoniacal liquid effervesced, and the escaping ammonia gas completely drove away the air from the tube in a few minutes, when the latter was sealed up at the capillary. The tube was then shaken violently so as to break the small bulb in it. The shaking was continued for a few minutes in order to ensure the complete liberation of the nitrogen. After the completion of the reaction the tube was opened under water, which had been previously boiled to expel the dissolved air, and the nitrogen was transferred into a graduated tube and measured. The volume of nitrogen, reduced to 0° and 760 m.m., amounted to 11.3 c.c., while, according to the equation given above, it ought to have been 12.2 c.c.

We may, therefore, conclude that the equation actually represents the reaction which takes place between the sulphoxime and ammonia. The small deficiency of nitrogen can readily be

accounted for by the solubility of this gas in the liquid and also by the incompleteness of the reaction under the conditions of the foregoing experiment.

When the ammoniacal liquid, in which the brisk reaction had taken place, was evaporated on a water-bath, small gas bubbles continued to appear until the liquid attained a syrupy consistency. On cooling, beautiful star-like clusters of pure ammonium m-benzenedisulphinate, consisting of elongated tetrahedra, separated out. This salt melts at 113°–115°, and the melting point was not altered by repeated crystallisation from water. There was nothing which indicated the presence of any other reaction products.

This method of changing a crude alkaline disulphonate into the oxime and then decomposing it by ammonia may be employed for the preparation of the pure disulphinate, in large quantities, which may, otherwise, be very difficult to obtain.

Ammonium p-benzenedisulphinate was obtained in the same way from the corresponding oxime. This substance crystallises in fine needles, and decomposes without melting at about 200°.

Benzene-monosulphoxime also yielded the ammonium salt of benzenemonosulphinic acid in good quantity.

Analytical data.

Ammonium m-benzenedisulphinate.

a) Nitrogen.

0.1421 gr. gave 13.1 c.c. of moist nitrogen at 14° and 763 m.m.

Nitrogen found	10.8%
Calculated for $C_6H_4(SO_2NH_4)_2, H_2O$	10.9 „

b) Sulphur.

0.1272 gr. gave 0.2305 gr. barium sulphate.

Sulphur found	24.88%
,, calculated	24.82 ,,

Ammonium p-benzenedisulphinate.

a) Nitrogen.

0.0939 gr. gave 8.75 c.c. of moist nitrogen at 17° and 758 m.m.

Nitrogen found	10.7%
Calculated for $C_6H_4(SO_2NH_4)_2$, H_2O	10.9 ,,

b) Sulphur.

0.0966 gr. gave 0.1729 gr. barium sulphate.

Sulphur found	24.6%
,, calculated	24.8 ,,

The silver salts of m- and p-benzenedisulphinic acids were also obtained. The former is crystalline, while the latter is amorphous and difficult to purify. Silver m-benzenedisulphinate was analysed with the following result:

0.0900 gr. gave on ignition 0.0466 gr. of metallic silver.

Silver found	51.8%
Calculated for $C_6H_4(SO_2Ag)_2$	51.4 ,,

The zinc salt of the meta-acid is soluble, but that of the para-acid is only slightly soluble in water.

The peculiarity of the reaction between the sulphoxime and ammonia reminds one of the decomposition of ammonium nitrite

on heating. It may be that the oxime forms an unstable ammonium salt, which soon decomposes into the sulphinic acid, nitrogen and water. The similarity of the reaction makes it probable that the sulphoximes are the substitution products of nitrous acid and not of hydroxylamine. The difficulty of their hydrolysis into hydroxylamine and the corresponding sulphonic acid seems to support this view.

When m-benzenedisulphoxime was treated with fuming nitric acid, it dissolved to some extent. On diluting the solution with water the oxime was reprecipitated unchanged. But when the nitric solution was allowed to stand for four or five days the colour of the fuming nitric acid had faded a little, and small crystals made their appearance on the surface of the liquid and on the sides and bottom of the vessel. The crystals dissolved readily in water, and the solution behaved as that of an acid. On neutralisation with caustic soda, a crystalline precipitate of a difficultly soluble sodium salt was formed. This precipitate was collected, recrystallised from hot water, and analysed. The amount of water of crystallisation, sodium, nitrogen, and sulphur found, as well as the form of the crystals, left no doubt as to its identity with the sodium salt of m-benzenedisulphimide. The formation of the imide in this case was, indeed, a surprise, and it was thought possible that the crystals first formed in fuming nitric acid might have been a complex compound, which gave rise to the imide on hydrolysis. In order to settle this point the crystals were dried upon a porous tile, then in a desiccator containing strong sulphuric acid and caustic soda, and a weighed quantity of the substance was titrated with $\frac{1}{10}$ N soda solution. The titer agreed exactly with that calculated

for the imide, showing that the crystals were nothing but the pure imide.

p-Benzenedisulphoxime also gave a similar result. This substance is almost insoluble in fuming nitric acid; yet, on allowing the mixture to stand from five to ten days a small quantity of the compound was changed into the corresponding imide. Although the quantity produced was so small that it was difficult to isolate it, its presence could be proved by the formation of the almost insoluble potassium salt on neutralising the diluted solution with caustic potash.

A notable quantity of sulphuric acid was found in the nitric solution in both cases. This is perhaps due to the complete decomposition of the oximes.

The unexpected reducing action of fuming nitric acid upon the disulphoximes here observed may be due to the lower oxides of nitrogen which exist in the acid. But further investigation is necessary to settle the question.

In concluding this communication, the author desires to express his great obligation to Prof. HAGA, who has taken a great interest in the work and aided him with valuable advice.