

Hydroxylamine- $\alpha\beta$ -Disulphonates (Structural Isomerides of Hydroximosulphates or Hydroxylamine- $\beta\beta$ -Disulphonates).

By

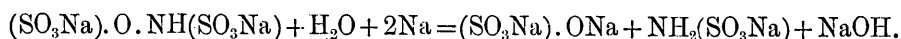
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In a previous paper (this Journ. 19, Art. 15), it was shown that Fremy's *metasulphazilate*, which till then had been considered to be constituted as an amine oxide, $O : N(SO_3K)_3$, is in reality a *hydroxylaminetrisulphonate*. The nature of the products of the proximate hydrolysis of the metasulphazilates seems to afford the strongest additional evidence that these salts are hydroxylaminesulphonates and, as such, mixed anhydrides of an acid-sulphate and a hydroxylaminedisulphonate.

The ultimate hydrolysis of a hydroxylaminetrisulphonate, through intermediate stages, into hydroxylamine and an acid sulphate, is difficult to carry to completion (this Journ. 19, Art. 15, 28), but the first stage of it, into a hydroxylaminedisulphonate and one-third of the quantity of acid-sulphate that is produced in the ultimate hydrolysis, is very easily accomplished. The hydroxylaminedisulphonate thus obtained proves to be an entirely new salt, structurally isomeric with the corresponding *hydroxylaminedisulphonate* (Fremy's *sulphazotate*), from which it differs greatly in

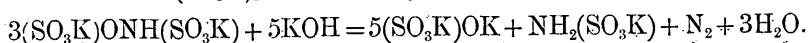
essential physical and chemical properties. The one is a $\beta\beta$ -derivative, the other an $\alpha\beta$ -derivative of hydroxylamine. Which is which is determined by the behaviour of the two salts towards sodium amalgam. A salt of the series already known remains unaffected, whilst one of the new series decomposes (p. 12) into sulphate and aminemonosulphonate (sulphamate, aminosulphate), just as its parent salt, hydroxylaminetrisulphonate, decomposes, in like circumstances, into sulphate and aminedisulphonate (iminosulphate). It must, therefore, have the $\alpha\beta$ -constitution, as shown in the following equation, framed to express its decomposition by sodium :



and the other salt have the $\beta\beta$ -constitution which it has always been assumed to have, $\text{HON}(\text{SO}_3\text{Na})_2$. The activity of the $\alpha\beta$ -salts towards sodium amalgam serves also to demonstrate their sulphatic constitution (derived from that of the hydroxylaminetrisulphonates) as the mixed anhydrides* of an acid-sulphate and a hydroxylaminemonosulphonate.

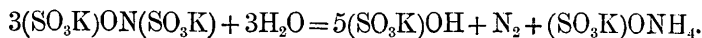
The action of potassium hydroxide upon the two salts seems clearly to establish the difference there is in their constitution. The old salt reverts to nitrite and sulphite when it is left, even in the cold, in a concentrated solution of the alkali (this Journ. 7, 40), whereas the new salt is only incompletely decomposed into sulphate, aminemonosulphonate, and nitrogen (p. 13), after several hours' digestion at 100–125° with the alkali. These results are exhibited by the following equations, the upper for the old or $\beta\beta$ -salt and the lower for the new or $\alpha\beta$ -salt :

* Two other examples of such mixed sulphatic anhydrides are any hydroxylaminetrisulphonate and any hyponitrososulphate. Raschig has recently adduced evidence (*Zeit. angew. Chem.*, 1905, 18, 1309) that nitrosyl sulphate is, after all, not a sulphate but a nitrosulphonate, $\text{O}_2\text{N}\cdot\text{SO}_3\text{H}$.



The lower of these equations recalls the action of heated alkalis upon hydroxylamine (Lossen) and upon hydroxylaminemonosulphonate (Claus). The upper equation brings out strongly the oximidic constitution of the $\beta\beta$ -salt.

It is an interesting fact that the course of the hydrolysis of the two salts in acidified solution is widely different, but it is a fact which cannot apparently be used to establish the nature of the difference in their constitution. The $\beta\beta$ -or long-known salt, by losing one of its two sulphonate groups, readily passes into the hydroxylamine- β -monosulphonate, $\text{HONH}(\text{SO}_3\text{K})$; whereas the new or $\alpha\beta$ -disulphonate passes (p. 15), much less easily, into acid sulphate and hydroxylamine itself (and products of its well-known decomposition), without ever affording evidence of any production of a monosulphonate, which in this case should have the α -constitution; expressed by $(\text{SO}_3\text{K})\text{ONH}_2$, and, as an amidogenium salt, be perhaps incapable of existence. The slowness with which an $\alpha\beta$ -salt begins to hydrolyse is illustrated by the fact that a solution of the potassium salt will remain clear for five minutes at the common temperature after it has been mixed with hydrochloric acid and barium chloride, whereas a solution of the $\beta\beta$ -salt will almost at once begin to show turbidity. When the hydrolysis of the $\alpha\beta$ -salt proceeds in the absence of much or any hydrochloric acid, nitrogen and ammonia very largely take the place of the hydroxylamine which is obtained in nearly the theoretical quantity when the salt hydrolyses in presence of a sufficiently concentrated hydrochloric-acid solution. The following equation expresses what principally happens in the absence of hydrochloric acid:



Silver oxide and lead peroxide seem to be without action upon the $\alpha\beta$ -salts in solution; they certainly do not produce the deeply coloured peroxyaminesulphonate which so strikingly results from their action upon the $\beta\beta$ -salts. This difference accords with that indicated in the constitution of the two series of salts. A hydroxylamine- $\alpha\beta$ -disulphonate also unexpectedly agrees with a hydroxylamine- $\beta\beta$ -disulphonate in not reducing copper or silver oxide in alkaline solution and is also inactive upon a solution of iodine in presence of sodium acid-carbonate. A hydroxylaminemonosulphonate, $\text{HONH}(\text{SO}_3\text{K})$, which, like it, has an aminic hydrogen atom in its constitution has the activity of hydroxylamine upon both alkaline copper solution and upon alkali-bicarbonate iodine solution.

Like the $\beta\beta$ -salts the hydroxylamine- $\alpha\beta$ -disulphonates decompose with gentle explosion when heated. Also, like the $\beta\beta$ -series, that of the $\alpha\beta$ -disulphonates includes highly alkaline normal salts, such as $(\text{SO}_3\text{K})\text{ONK}(\text{SO}_3\text{K})$ and $(\text{SO}_3\text{Na})\text{ONNa}(\text{SO}_3\text{Na})$.

A concentrated solution of the disodium salt is not precipitated by silver nitrate, mercuric nitrate, lead nitrate, or barium chloride. A concentrated solution of basic lead acetate precipitates from it an oil, which becomes crystalline on standing. A concentrated solution of a potassium salt precipitates from it the very much less soluble potassium salt. Barium hydroxide gives a voluminous, apparently amorphous, precipitate, probably of a sodium barium salt.

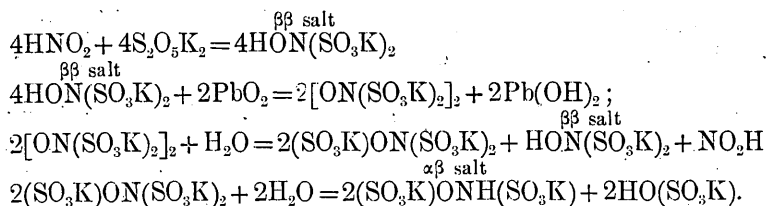
The molecular magnitude of the normal or trisodium hydroxylamine- $\alpha\beta$ -disulphonate. (p. 11), as determined cryoscopically by means of melted Glauber's salt (Löwenherz), is that expressed by $\text{O}_7\text{NS}_2\text{Na}_3$, the same, therefore, as that found for the normal

sodium $\beta\beta$ -salt (this Journ. 19, Art. 15, 33). Remarkably, however (and it is a unique experience with this method, so far as has been ascertainable), the depression of the solidifying point of the sodium sulphate is at first much less than that which corresponds with the simple molecular weight, the number for which it only reaches and remains steady at, in the course of an hour or two and after several repetitions of remelting and solidifying. It would seem from this that the solid salt consists of associated simple molecules which require time to separate from each other after dissolution in melted Glauber's salt.

The discovery of this new series of salts, establishing as it does the existence of significant structural isomerism in other than carbon compounds, should prove to be of very special interest, there being hardly any other instance known, except that of nitramine with hyponitrous acid, the existence of which is disputed by Hantzsch (*Zeit. unorg. Chem.*, 1898, 19, 106) just because it would be the only case known in inorganic chemistry.

The subjoined scheme of equations may serve to show at a glance the relation by derivation of the new series of salts to the old series. A hydroxylamine- $\beta\beta$ -disulphonate, a salt formed by the union of nitrous acid with a metasilphite, is oxidisable wholly into a peroxyamine-sulphonate. This, by hydrolysis in presence of an alkali, becomes, to the extent of half its nitrogen, hydroxylaminetrisulphonate; to the extent of a fourth of its nitrogen, the $\beta\beta$ -salt again; and, to the extent of the remaining fourth of its nitrogen, nitrous acid (nitrite) again. Lastly, by acid hydrolysis, the hydroxylaminetrisulphonate becomes sulphate and a hydroxylamine- $\alpha\beta$ -disulphonate. From this it will be seen that, at most, only the half of the $\beta\beta$ -salt comes out as the $\alpha\beta$ -salt,

one-fourth of it being regenerated and the remaining fourth reverting to its parent salts, of which the sulphite has suffered oxidation to sulphate.



The return of an $\alpha\beta$ -salt to the state of its $\beta\beta$ -isomeride can hardly be looked upon as possible, its own production having been due to oxidation of a fourth of the sulphonate groups into acid-sulphate.

Salts

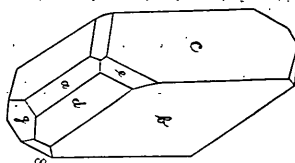
Dipotassium Hydroxylamine- $\alpha\beta$ -disulphonate,— $(\text{SO}_3\text{K})\text{ONH}(\text{SO}_3\text{K})$.—Potassium hydroxylaminetrisulphonate, dissolved in ten times its weight of warm water (it is much less soluble in cold water, this Journ. 19, Art. 15, 8), soon begins to hydrolyse when its solution is quickly cooled and mixed with a drop of dilute sulphuric acid just before it would otherwise crystallise out again. The hydrolysis, to the end of its first stage, is complete in about four days. When the solution is deprived of sulphate and neutralised by the addition of barium carbonate or hydroxide, filtered, and evaporated, the new disulphonate is obtained in crystals, to the extent of at least two-thirds of the calculated yield. That hydrolysis of the trisulphonate proceeds to the extent shown in the equation (see above) in about four days and then proceeds much more slowly, has been ascertained both acidimetrically and by estimation of the sulphuric acid produced.

The dipotassium salt is an anhydrous salt, about twice as

soluble in water as the corresponding (but hydrated) $\beta\beta$ -salt. Of it 6.44 parts at 16.4°, 7.18 parts at 17.8°, and 8.05 parts at 20° dissolve in 100 parts of water. Its solution is neutral to litmus, to methyl-orange, and to phenolphthalein.

The salt forms hard monoclinic prisms which are sometimes short thick prisms, sometimes flattened tables, and sometimes long slender prisms or needles. Crystals of the one or other habit generally recrystallise in that habit but the salt is not dimorphous. A saturated solution of one form of the salt is saturated also towards another form of it, whilst the two forms will lie side by side unchanged for a length of time in the same mother-liquor. Prof. Jimbō has kindly supplied the following account of his examination of a short thick prism:—A monoclinic crystal, developed perfectly on one end of the clinodiagonal, about 6 mm. long, was measured by means of a contact goniometer, only two angles, c and e , having been measured by reflection. The faces a and g were depressed; the other faces also did not give good images. Seven faces were recognised; one other could not be determined.

a.	$\infty P\infty$	bd	=	133°25'
b.	$\infty P\infty$	ce	=	144°27'
c.	$\circ P$	cf	=	127°53'
d.	∞P	ed	=	141°25'
e.	$-P$	df	=	126°15'
f.	$P(?)$	cg	=	117°
g.	$\frac{1}{4} P\infty(?)$			



The results of analyses of (A) the tabular form and of (B) the acicular form of the salt, are as follows:

A.	.2863	gave .1845	potassium sulphate.	Potassium	=	28.98
	.2105	gave .3673	barium sulphate.	Sulphur	=	23.96

	.2739 gave 12.58cc moist nitrogen at 19.5° and 756.1mm.	Nitrogen = 5.22
B.	.2679 gave .1751 potassium sulphate.	Potassium = 28.74
	.2684 gave 11.9cc. moist nitrogen at 16.7° and 765.5mm.	Nitrogen = 5.19

$\text{HO}_7\text{NS}_2\text{K}_2$ requires potassium, 29.06; sulphur, 23.79; nitrogen, 5.21 per cent. In all analyses given in this paper sulphur was determined by heating the salt with hydrochloric acid in a sealed tube at 180 for five hours or at 200° for two hours.

Tripotassium Hydroxylamine- $\alpha\beta$ -disulphonate, $(\text{SO}_3\text{K})\text{ONK}(\text{SO}_3\text{K})_2\text{H}_2\text{O}$.—This salt is precipitated, at first as an oil, when alcohol is added to its concentrated aqueous solution, prepared by dissolving the disulphonate in a little hot water and adding to it the calculated quantity of potassium-hydroxide solution. The oily salt slowly solidifies into lumps of microscopic crystalline plates. The quantity obtained should be about equal in weight to that of the disulphonate used, the calculated quantity being five parts from four. It is very soluble in water. Its solution is not precipitated by barium chloride, in this respect being unlike a solution of the corresponding $\beta\beta$ -salt. It is caustic in taste, and explodes suddenly when heated.

Analysis:	.1696 gave .1286 potassium sulphate.	Potassium = 34.05
	.2588 gave .1944 potassium sulphate.	Potassium = 33.73
	.1568 gave .2343 barium sulphate.	Sulphur = 20.52

$\text{H}_4\text{O}_9\text{NS}_2\text{K}_3$ requires potassium, 34.18; sulphur, 18.66 per cent

The *disodium salt*, $(\text{SO}_3\text{Na})\text{ONH}(\text{SO}_3\text{Na})$, is like the $\beta\beta$ -salt, anhydrous. The very soluble sodium hydroxylaminetrisulphonate is dissolved in five times its weight of water and acidified with dilute sulphuric acid. In two or three days at the ordinary temperature it will have all hydrolysed and the solution is then

to be neutralised with sodium carbonate. On exposure for a night in the ice-chamber, almost all the sodium sulphate will crystallise out and then the mother-liquor can be evaporated to get the new salt. Like corresponding $\beta\beta$ -salt, this salt forms hard masses firmly adhering to the sides of the vessel. These masses are stellar or warty groups of microscopic thick rhombic plates. The salt is exceedingly soluble in water, from which it can be nearly all precipitated by alcohol. Two preparations of the salt were analysed (I. and II):

I.	.2209 gave .1313 sodium sulphate.	Sodium = 19.28
	.1059 gave .2096 barium sulphate.	Sulphur = 27.17
	.5151 gave 26.45 cc. moist nitrogen at 17° and 756.8mm.	Nitrogen = 5.94
II.	.2509 gave .1502 sodium sulphate.	Sodium = 19.41
	.0959 gave .1910 barium sulphate.	Sulphur = 27.35
	HO ₇ NS ₂ Na ₂ requires sodium, 19.43; sulphur, 27.02; nitrogen, 5.92 per cent.	

The *trisodium salt*, (SO₃Na)ONNa(SO₃Na),2H₂O, is prepared just in the same way as the tripotassium salt. It is obtained as a crystalline powder. For determination of its molecular magnitude, see p. 11.

	.1450 gave .1054 sodium sulphate.	Sodium = 23.57
	.2269 required 7.56cc. N/10hydrochloric acid with methyl-orange as indicator.	Alkalinity as sodium = 7.66
	.3594 gave .5698 barium sulphate.	Sulphur = 21.75
	H ₄ O ₉ NS ₂ Na ₃ requires sodium, 23.41; alkalinity sodium, 7.8; sulphur, 21.71 per cent.	

Diammonium salt, (SO₃NH)ONH(SO₃NH₄).—Ammonium hydroxylaminetrisulphonate (this Journ. 19, Art. 15, 9 hydrolyses

in the same way as the sodium salt. The ammonium acid-sulphate is got rid of by adding just enough barium hydroxide solution, filtering, and evaporating, at first at a gentle heat and then in the cold over sulphuric acid under reduced pressure. It occurs as small thick plates, which are somewhat hard, and as nodules composed of minute tabular crystals. It is a very soluble salt, 3 parts dissolving normally in just 2 parts of water at 18°, but it is very apt to form supersaturated solutions. It is a more stable salt than the corresponding $\beta\beta$ -salt. Its crystals are probably anhydrous, but those analysed showed the presence of 0.25 H₂O per molecule.

.3559 gave .7189 barium sulphate. Sulphur = 27.74

.2320 gave 35.5cc. moist nitrogen at

16.2° and 754.5mm. nitrogen = 18.18 per cent.

H₉O₇N₃S₂ requires sulphur, 28.21; nitrogen, 18.53. With $\frac{1}{4}$ H₂O added, it requires sulphur, 27.66; nitrogen 18.17 per cent.

Barium salts.—Barium salts have not been prepared in a state suited for satisfactory determination of their nature. Evaporation of a solution of the ammonium salt with excess of barium hydroxide in a vacuum over sulphuric acid to a small volume removed all ammonia. After removal of the excess of barium hydroxide by carbon dioxide, the filtered solution was further evaporated in the desiccator. First, a viscid liquid and then a bulky friable, porous mass, devoid of crystalline character, were obtained. The latter was not quantitatively analysed but it yielded, when hydrolysed, barium sulphate and hydroxylamine sulphate in crystals which were further identified by a very satisfactory sulphuric acid determination. The product was therefore undoubtedly a barium-hydroxylamine- $\alpha\beta$ -disulphonate. By using less barium hydroxide, crystallised ammonium barium salts of varying composition may

be obtained. One quantitatively examined had a composition corresponding fairly well with that of a compound of 6 mol. of the diammonium salt with 1 mol. of the $\frac{2}{3}$ -normal barium salt.

Molecular Magnitude of Trisodium Hydroxylamine- $\alpha\beta$ -disulphonate.

By Löwenherz's method, the molecular magnitude of the trisodium hydroxylamine- $\beta\beta$ -disulphonate has been found to be (anhydrous) 233 and 239.6, whilst $O_7NS_2Na_3$ requires 259.35 (this Journ. 19, Art. 15, 33). By the same method, the following approximations to the same number have been obtained for the $\alpha\beta$ -salt, namely, 269.6, 279.3, and 256.4, using the constant, 32.6, for sodium sulphate found by Löwenherz. The details of these determinations of the molecular magnitude of the $\alpha\beta$ -salt are specially interesting (p. 4). Of this salt, .8371, dissolved in 40.48 melted Glauber's salt, produced a depression of 0.22° in the crystallising point, corresponding with the mol. weight, 306.2. After solidifying and melting three times, the depression reached 0.24° and remained at that, which corresponds with 269.6. There was now added .5848 more of the salt, and the depression due to this addition was at first only $.005^\circ$, corresponding with a mol. weight of 9416, that is, about 40 times the normal magnitude. On allowing the mixture to solidify and remelt, the depression grew in amount until at the sixth repetition it reached its maximum, corresponding with the simplest formula of the salt. The whole quantity, 1.4219 now caused a depression which gave the mol. magnitude as 279.3. Adding now .9026, the additional depression was at first only $.04^\circ$, corresponding with a mol. weight of 1878 which is about 8 times the simple molecule. But, again as

before, after several times repeated melting and solidifying, the normal depression was reached and remained constant, and the total quantity of the salt, namely, 2.3245 gave a depression of 0.73° , indicating the molecular magnitude, 256.4.

Reduction of the Disodium Salt by Sodium Amalgam.

Disodium hydroxylamine- $\alpha\beta$ -disulphonate, .4811 gram, was shaken with 12 grams of 3 per cent. sodium amalgam (which acts very slowly on it) and left with it, with occasional shaking, for three days. Much sodium remained unconsumed. The solution was rendered neutral to phenolphthalein by acetic acid and the sulphate present precipitated as barium sulphate. Of the sulphur in the quantity of salt taken, 13.73 per cent. were thus found as sulphate, instead of 13.51, the calculated third. The aminemonosulphonate in the filtrate from this sulphate was hydrolysed by heating the solution at 150° for three hours in a sealed tube with hydrochloric acid. It thus yielded the rest of the sulphur as sulphate, a result which, effected at such a temperature, showed that that sulphur was all in direct union with nitrogen and that none of the hydroxylaminedisulphonate had been left undecomposed by the sodium. As a check, the ammonia, the other product of the hydrolysis of the aminemonosulphonate, was also determined and found equal to 5.5 per cent. instead of 5.94 per cent., the full amount. The production of aminemonosulphonate by the reduction of the hydroxylamine- $\alpha\beta$ -disulphonate was further established quantitatively in a separate experiment, in which, after the reduction, the aminesulphonate was precipitated characteristically by mercuric nitrate and the acid itself, after recovery from its mercury salt, crystallised out and otherwise tested.

*Decomposition of the Potassium Salt by
Potassium Hydroxide.*

Whether potassium hydroxylamine- $\alpha\beta$ -disulphonate is decomposed solely into acid-sulphate, aminomonosulphonate, and nitrogen, when heated with a concentrated solution of potassium hydroxide (p. 3), or whether it is, to a small extent, decomposed into nitrous oxide, according to the equation,—



is not certain. It is experimentally difficult to get sufficiently trustworthy qualitative results. Even qualitatively, there is the uncertainty to deal with, as to the entire absence of nitrous oxide from the nitrogen obtained. In these experiments, the gas given off extinguished a flaming match and refused when mixed with hydrogen to explode by the electric spark. The occasional production of some nitrous oxide is, perhaps, to be inferred from the ratio of the quantity of sulphur as sulphate to that as aminomonosulphonate found in one experiment, although its production was not thus indicated in another experiment. But, as accuracy in determining this ratio is affected by the fact that the analytic separation of sulphate from aminomonosulphonate is only approximate (this Journ. 9, 281-2; 13, 503-6), the production of any nitrous oxide still remains uncertain. Another difficulty in the quantitative examination of the decomposition is that the decomposition is far from complete after several hours heating at 120°. The presence of still undecomposed salt is shown by the production of hydroxylamine when the products are hydrolysed and by the fact that a temperature of 180°, instead of 150°, is necessary to ensure complete hydrolysis of the products.

No ammonia is generated, the only products being those already mentioned.

When the gases were to be collected the salt was heated with one and a half to twice its weight of potassium hydroxide and about four times its weight of water for six hours at 100° or for four hours at 120° in a tube retort connected with a Sprengel pump. Needless to say, explosive ebullition and corrosion of the hard glass tube (rendering it opaque) had to be encountered as difficulties. When the gases were to be allowed to escape, the mixture was heated in a platinum dish on the water bath. For analysis, the residue in either case was made faintly acid to phenolphthalein by nitric acid, and sulphate then precipitated by barium nitrate. The thoroughly washed precipitate was purified in the usual way by fusion with an alkali carbonate before weighing. The aminesulphonate was precipitated by mercuric nitrate, the mercuric salt was hydrolysed, and the sulphuric acid and sometimes the ammonia resulting were determined. The filtrate from the mercury precipitate always showed the presence of hydroxylamine- $\alpha\beta$ -disulphonate.

In an experiment with 1.057 gram of salt, the sulphur found as sulphate was 66.82 per cent., and that as aminesulphonate 15.73 per cent. of the total sulphur, leaving 17.45 to be accounted for as undecomposed salt. Of the total nitrogen, 29.64 per cent. were got as ammonia from the aminesulphonate, and 48.89 per cent. as gas (27.85 cc. moist nitrogen at 18° and 639.8 mm. = .002692), leaving 21.47 per cent. as undecomposed salt. The difference between 17.45 and 21.47, perhaps due to slight leakage of air into the apparatus during the six hours heating, is not at all so significant as it is made to appear by the way of stating the results, the total percentage of nitrogen in the salt being only

5.2 per cent. On the assumption that 65 per cent. of the salt decomposed so as to give nitrogen (p. 3), and 16.7 so as to give nitrous oxide (p. 13), and that 18.3 per cent. remained undecomposed, the numbers should be sulphur as sulphate, 66.68, and as amine-sulphonate, 15.01 per cent., nitrogen as amine-sulphonate, 30.02, and as free nitrogen and nitrous oxide, 48.30 per cent., of the total.

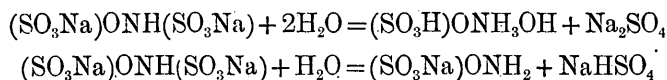
In another experiment, in which .9792 salt was heated at 120–125° for four hours, the indications of the analysis were that 19.9 per cent. of the salt had resisted decomposition and that no nitrous oxide had been formed. The numbers obtained were 66.69 per cent. sulphur as sulphate, instead of 66.75 calculated; and 12.94 sulphur as amine-sulphonate, instead of 13.35 calculated. Some of the gas was lost, so that the distribution of the nitrogen could not be sufficiently tested.

In an experiment, in which the salt was heated at 100° with potassium hydroxide for many hours in a platinum dish with occasional renewal of the water, the sulphur of the sulphate produced amounted to 77.24 per cent. of the total. Decomposition of all the salt with production of nitrogen would give 83.33 per cent.

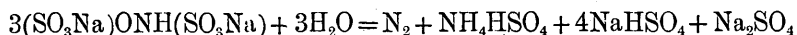
Products of Hydrolysis of Hydroxylamine- $\alpha\beta$ -disulphonates.

Potassium hydroxylaminetrisulphonate, which for these experiments could be substituted for the disulphonate, the product of its hydrolysis, was moistened with dilute sulphuric acid and heated in a vacuum at 100°, in order to effect its hydrolysis and collect the gas evolved. The gas had no action upon ferrous sulphate, and was not appreciably soluble in alcohol. It therefore contained no nitric oxide and apparently no nitrous oxide.

Sodium hydroxylaminetrisulphonate in solution in water, just acid with sulphuric acid, was left for several days to slowly hydrolyse, principally to the disulphonate. It was then kept for fifty minutes at 95°, during which brisk effervescence of nitrogen went on, slackening only when near the end of the time. The acidity was then found to be somewhat more than that indicated by either of the following equations, the one for hydroxylamine sulphate, the other for the unknown hydroxylamine- α -monosulphonate:



The additional acidity and the escape of nitrogen indicated the occurrence, to some extent, of the decomposition expressed by:—



The solution gave only a moderate reaction for hydroxylamine with the copper test, and on evaporation, with or without previous neutralisation, gave nothing but sodium and ammonium sulphates.

In presence of sufficient hydrochloric acid, say, one volume of the fuming solution to ten volumes of solution of the salt, the production during hydrolysis of nitrogen and ammonia is very slight. The disodium salt in such a solution, after it had been kept heated for five minutes or so by immersing the vessel in boiling water, gave evidence, on titrating with iodine, of the presence of hydroxylamine equivalent to 95 per cent. of the salt. In another experiment, in which the solution was left standing for 50 days at the ordinary temperature, 76.5 per cent. of the salt had then yielded hydroxylamine.

In another similar experiment, the solution after standing in the cold was also evaporated in the cold under reduced pressure, until the salts crystallised out, and still nothing else but sodium

and hydroxylamine sulphates, except a very little ammonium sulphate, was obtained.

In other experiments, using in these cases the dipotassium salt, the hydrolysis was allowed to go on either in the cold or at 60°, and portions of the solution occasionally tested to see whether some indication could be got of the production of hydroxylamine- α -monosulphonate at any stage of the hydrolysis. In making the test, the acid sulphate was removed by barium chloride and the solution then tested with iodine in presence of sodium acid-carbonate. Since the consumption of the iodine caused no precipitation of barium sulphate, evidence was thus obtained that the reducing substance was hydroxylamine only and not its sulphonate derivative. Ultimately, by evaporating the solution, when sufficiently hydrolysed, hydroxylamine sulphate was crystallised out, along with the sodium sulphate.
