Oxyamidosulphonates and their Conversion into Hyponitrites.

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In our paper on the *Reaction between Sulphites and Nitrites of Metals other than Potassium, (J. Ch. Soc.* **51**, *659)*, we gave notice of our intention to work upon the reactions of the sodium salts. This intention we have carried out, and already find ourselves in a position to materially extend and modify the knowledge of the chemistry of the sulphazotised compounds contained in the writings of our predecessors in the investigation, Fremy[*], Ad. Claus and Koch[†], Berglund[||], and Raschig[‡]. We propose to publish our contribution to this large subject in a few short papers, such as the present one, each complete in itself.

Oxyamidosulphonates, the subject of the present paper, are the *sulphazidates* of Fremy, the *sulphydroxylamates* of Claus, the *hydroxylamine-monosulphonates* of Raschig. Between the one set of terms—

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[*] *Ann. Chim. Phys.* [3], **15**, 408.

[†] *Ann. Chem. Pharm.* **152**, 336; **158**, 52 and 194.

[||] *Bull. Soc. Chim.* **25**, 455; **29**, 422; *Ber. Ch. Ges.* **9**, 252 and 1896.

[‡] *Ann. Chem.* **241**, 161.

nitrilo–, *imido–*, and *amido–*, *oximido–* and *oxyamidosulphonate*, and the other set— *amine–* and *hydroxyamine–tri–*, *di–*, and *monosulphonate*, there is not much to choose by. But as it is desirable on the score of consistency, to employ exclusively one set or the other, the already prevalent use of *nitrilo–*, *imido–*, and *amidosulphonate* makes it proper to use *oximido–* and *oxyamidosulphonate* rather than *hydroxyamine–di–* and *monosulphonate.*

Oxyamidosulphonic acid, known only in solution, was first prepared by Fremy, who found that *potassium oximidosulphonate, (neutral-sulphazotate)*, sooner or later decomposed into acid-sulphate and the oxyamido-salt, doing so at once when its solution was boiled. Altering his atomic weights to those now accepted, and writing empirically his formulæ, to which he attached no constitutional significance, his equation becomes —

$$S_5O_{20}K_4H_{10}N_2 = S_2O_8K_2H_6N_2 + 2KHSO_4 + H_2SO_4{}^*$$

Claus has shown, however, that these formulæ incorrectly represent the composition of the salts, and Raschig has confirmed Claus's statement. The two formulæ corrected and halved stand as $S_2O_9K_2H_5N$ and SO_4KH_2N, or $HON(SO_3K)_2(OH_2)_2$ and $HONH(SO_3K)$, according to Claus. The latter formula we have further to modify slightly.

To get the oxyamidosulphonic acid pure for preparing its salts, Fremy neutralised with ammonia the hydrolysed solution of potassium oximidosulphonate, added barium chloride, filtered off sulphate, and then, by adding baryta-water, precipitated a dibarium oxyamidosulphonate. This salt, when washed, he decomposed by adding just enough sulphuric acid to combine with the barium, and then used the filtered solution of the new acid for combining with bases. The acid appears

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He recognised the peculiarity and importance of this first instance of what we now style the hydrolysis of a sulphonate into a sulphate.

to be the only sulphoxyazotised acid possessing any stability. Claus introduced the slight modification of Fremy's process for preparing it of omitting the preliminary neutralisation with ammonia.

Having discovered a second barium salt, neutral and soluble, we proceed differently in treating the barium precipitate, and thereby avoid the contamination of the salts with sulphite, always present in Fremy's barium precipitate (see the section of this paper headed, *the decomposition of oxyamidosulphonates by alkaline bases).* The dibarium salt is, as found by Fremy, very alkaline to litmus, and we add to it only enough sulphuric acid to get a neutral solution, along with barium sulphate equivalent to half the barium and such barium sulphite insoluble as may have been present in it. The solution contains only monobarium oxyamidosulphonate and from it can be prepared the acid and its salts by adding its equivalent of sulphuric acid or a sulphate, to determine which, an estimation of barium is made in a portion of the solution.

Raschig prepares an impure acid from Fremy's solution obtained by boiling potassium oximidosulphonate so as to hydrolyse it into potassium sulphate and oxyamidosulphonate. To do this he removes the potassium sulphate by alcohol and then concentrates the solution of the acid to a syrupy consistence.

Sodium oxyamidosulphonate, prepared by Fremy and by us, is a clear gummy liquid as thick as molasses, which exposed over sulphuric acid (in a partial vacuum) never solidifies or shows any sign of crystallisation. It is neutral in reaction.

Potassium oxyamidosulphonate, prepared and analysed by Fremy, by Claus, and by us. It occurs in six-sided plates as stated by Fremy, when crystallised from its hot solution, but the plates are more often square, while by spontaneous evaporation of its cold solution thick tables and bold prisms are obtained. Claus found the crystals to be anhydrous, and Fremy's analysis and formula agree with this finding. But it is now known that Fremy's analytical results cannot be relied on, and we have already had to give an instance of this in the present paper and shall have to give others. Differing from Claus, we find all the crystals of this salt to effloresce slowly over sulphuric acid, and to give on analysis results indicating the presence of one molecule of water. Solutions show a great tendency to supersaturate, and it becomes often quite difficult to crystallise them. When thoroughly dry the crystals can be kept for months without undergoing much change, but moist they are unstable, hydrolysing and becoming acid to litmus. The acidity developed is that of hydroxyammonium sulphate, hardly showing with methyl-orange. Heated they suddenly intumesce below 100° and thoroughly decompose.

To determine the sulphur and nitrogen we hydrolysed the salt in a sealed tube with hydrochloric acid at 130° C., here following Raschig's process, which gives, however, somewhat irregular results as we afterwards found (see the analysis of the dibarium salt). The hydroxyamine thus produced was measured by iodine after addition of potassium acid-carbonate. Water could not be removed by exposure over sulphuric acid at the ordinary temperature and pressure rapidly enough to be convenient for analytical purposes, this and other sulphazotised salts retaining, according to our experience, part of their crystallisation-water with great tenacity. Nor could the water be well expelled in the oven, because of the decomposition of the salt at about 95°. But we made a fairly good estimation of it, by moderately heating the salt in a Sprengel-pump vacuum, in a long bulbed tube containing also sulphuric acid. The following is a table of our results—

	$HONH(SO_3K),OH_2$	*a*	*b*	*b*
Potassium	23.08	22.53*	23.45	
Sulphur	7.58	7.34	7.69	7.56
Oxyamidogen, HONH,	18.94	17.96	19.76	17.50
Water	10.39		9.29	

Sample *a* was in prisms, and *b* in tabular crystals. We have given much consideration to Claus's apparently carefully obtained results, but are unable to offer any explanation of their difference from ours. We have prepared the salt in winter and in summer (when he found it difficult to work), by evaporation of cold solutions and by cooling hot solutions, and have always obtained crystals which slowly effloresced in the desiccator.

Dibarium oxyamidosulphonate, prepared by Fremy and by us, is a crystalline, alkaline, nearly insoluble salt. It dissolves in hydrochloric acid, and then shows by the odour evolved, the presence of sulphite, from a trace only to even much, as an impurity. The only analytical datum given by Fremy is that the salt is formed from one equivalent of acid and two equivalents of baryta. We have analysed it and found for it a composition agreeing with the formula given by Fremy less the H_2 by which his formulæ generally exceed those now adopted.

In this analysis and that of the following salt we slightly modified the method of hydrolysing, so as to get uniform and higher numbers for the hydroxyamine. The modification consisted in heating for some time with hydrochloric acid only to 100^0, before raising the temperature to 130^0. Simple hydroxyammonium sulphate may be rapidly heated with acid to 130^0 or even higher without getting low results, from which it would appear that at the moment of its formation at 130° from its sulphonic derivative, hy-

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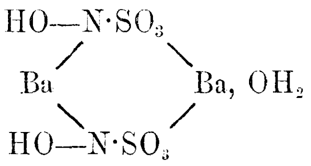
* Slight loss of potassium sulphate during cooling known to have occurred.

droxyamine is less stable than when already formed. The constitution of the dibarium salt is expressed by the formula—



	Calculated.	Found.
Barium	53.31	53.13
Sulphur	12.45	12.41
Oximidogen, HON,	12.06	12.02

Barium oxyamidosulphonate, prepared by us, in solution first, as already described in this paper, by adding just enough sulphuric acid to the dibarium salt to remove half its barium. The neutral liquor thus obtained yields by evaporation over sulphuric acid crystals of the salt. It is a very soluble salt and forms small hard brilliant square tabular crystals, intermixed with minute square prisms. When long kept it decomposes. Its crystals contain water. Heated nearly to 100°, it suddenly and violently decomposes into gases and barium sulphate.

In analysing it the barium was determined in one case by igniting with sulphuric acid (*a*); in two cases the salt was slowly heated with dry sodium carbonate, whereby oxygen was absorbed from the air, after which the heat was raised to fusion of the mixture, and the barium and sulphur both determined (*b*); while in another case, the salt was hydrolysed by heating with hydrochloric acid, the separated barium sulphate (representing all the barium and half the sulphur of the salt) weighed, the other half of the sulphuric acid precipitated with barium chloride, and lastly the hydroxyamine titrated with iodine (*c*). The results were the following—

	$(HONHSO_3)_2Ba,OH_2$	*a.*	*b.*	*b.*	*c.*
Barium	36.15	36.17	36.27	35.88	35.53
Sulphur	16.88		16.84	16.65	16.49
Oxyamidogen,	16.88				16.50

The hydrolysis of oxyamidosulphonic acid.

Although oxyamidosulphonic acid possesses relative stability, the fact that its solution does decompose was fully noticed by Fremy. Raschig has found that the decomposition proceeds sharply and, in presence of hot acid, rapidly, according to the equation—

$$2HONHSO_3H+2H_2O=(NH_3OH)_2SO_4+H_2SO_4$$

and with this important finding we fully agree from experience, and to it have nothing to add. Fremy stated that when boiled with water the acid decomposes wholly into acid-ammonium sulphate and oxygen or hydrogen-peroxide. His finding ammonia and oxygen (or any gas) cannot be explained. He appears to have tested for hydrogen-peroxide by adding manganese binoxide, which would account for his finding it, since an effervescence of nitrous oxide could easily pass for one of oxygen.

Claus expressed his hesitation to accept Fremy's equation (modified)—$2HONH(SO_3H)+2H_2O=2(NH_4)HSO_4+O_2$, as quantitative, but at the same time admitted that he had also obtained (besides sulphuric acid) ammonia and oxygen (or nitrous oxide.) Raschig has got other results, as already stated, and in these both ammonia and either oxygen or nitrous oxide are absent. These inexplicable differences have their parallel in what is contained in the next section of this paper, only there the differences announced are between ourselves and the other workers.

In presence of potassium-acid-carbonate oxyamidosulphonates react with iodine solution like a hydroxyamine salt, only very much more slowly, so that without previous hydrolysis their amount can be titrated in this way though only with difficulty.

Decomposition of oxyamidosulphonates by alkaline bases.

The decomposition of oxyamidosulphonates by a solution of potassium hydroxide had apparently been fairly well worked out when we came to give attention to it. Fremy had observed that when heated with excess of this reagent the potassium salt disengaged ammonia, as well as oxygen of which, as he says, he had established the absolute purity by analysis. Hence it seemed that oxyamidosulphonates undergo the same decomposition when heated with alkali as when heated with acid.

Lossen had just discovered hydroxyamine when work upon the sulphazotised bodies was taken up by Claus, and this circumstance led the latter to see in the reaction between potassium hydroxide and Fremy's sulphazidate, as observed by Fremy and by himself, most convincing evidence that the salt is constituted as a sulphonic derivative of hydroxyamine, and decomposes with alkali into this base and potassium sulphate. He did not, he admits, succeed indeed in isolating the hydroxyamine or any of its salts, but he found all the sulphur of the sulphazidate converted into sulphate, and just the other bodies and in just the proportions which Lossen had found hydroxyamine to yield when heated with alkali, namely, ammonia equivalent to between a third and a half of the total nitrogen, and gases which neither extinguished nor rekindled a glowing match, which were, therefore, not the pure oxygen of Fremy's finding, and which might well be nitrogen mixed with nitrous oxide, as required on the supposition made. Added to this was the fact of the reducing action which the alkaline mixture exerted upon copper and silver, and the proof seemed complete.

Raschig, in his recent paper, went further in the matter than Claus and, with or without experimenting we cannot decide from his words, concluded that an (unheated) alkaline solution of oxyamidosulphonic acid is actually a solution of free hydroxyamine in the quantity calculated from the amount of the acid taken, and therefore just such a solution of hydroxyamine as is used and wanted for preparing aldoximes and acetoximes.

Now with the exception of nitrous oxide being given off, and that of reduction of copper and silver salts—an action to be treated of in the following section of this paper, none of the observations of these chemists have we been able to confirm. This decomposition of oxyamidosulphonates by alkali is of another and still more interesting character than Claus and Raschig conceived it to be. That the oxyamidosulphonates are hydroxyamine derivatives, which hydrolyse in *acid* solutions into hydroxyamine and sulphate, is indeed certain, as ascertained by Raschig. But, nevertheless, in *alkaline* solution they give neither sulphate nor hydroxyamine, nor the decomposition-products of hydroxyamine.

Oxyamidosulphonates decompose with potassium hydroxide, and similar reagents, exclusively into sulphite and hyponitrite, and the decomposition-products of a hyponitrite. No ammonia and, so far as we could judge, no sulphate and no nitrogen—or if any only unimportant quantities of nitrogen and sulphate—are formed. The difficulty of keeping a sulphite solution for days free from sulphate, and of detecting small amounts of nitrogen in presence of nitrous oxide are well-known facts sufficiently explaining any uncertainty in our assertions. The total absence of ammonia peremptorily forbids any admission of the generation of hydroxyamine.

Cold dilute alkali or alkaline-earth hydroxide suffices to partly effect the change under consideration. Consequently every attempt to form dipotassium or sodium oxyamidosulphonate corresponding with the dibarium salt has failed in our hands because of this resolution of the salt into simpler ones on adding alkali. Also for the same reason Fremy's dibarium salt, described in this paper, although an almost insoluble salt, cannot, we find, be prepared quite free from sulphite, and when kept for any considerable time becomes charged with it and with traces of hyponitrite.

To effect the complete or nearly complete conversion of these salts into sulphite and hyponitrite they may be either left for days in the cold with the very strongest potassium-hydroxide solution, or be heated to boiling for a short time with strong alkali. In both cases effervescence occurs, due to the decomposition of hyponitrite. The gas is not the feeble supporter of combustion met with by Claus, but so far behaves as oxygen, as Fremy had observed. Only it is not oxygen but nitrous oxide, soluble in water. The highly alkaline liquor when acidified gives abundance of sulphur dioxide, and when only neutralised gives with barium chloride a precipitate which might of course be taken for sulphate by a mind prepossessed as Claus's almost admittedly was, and which does, as is well-known, rapidly change into sulphate on the filter. When partially or fully neutralised with acetic acid the solution gives on treatment with sufficient silver nitrate much silver hyponitrite together with a very little reduced silver owing to the never quite complete destruction of the sulphonic salt. At first the silver nitrate is consumed in forming potassium-silver sulphite, and this consumption can be avoided if desired, either by using the barium salt instead of the potassium salt, or by adding barium hydroxide, and then filtering off barium sulphite before adding silver.

This decomposition actually furnishes much the most productive method of preparing hyponitrite yet discovered. The following are the results of some trials we have made, the silver hyponitrite having been purified by the authors' method (*J. Ch. Soc*, **45**, 81) of dissolution in nitric acid and reprecipitation with sodium carbonate. Generally the silver hyponitrite was directly weighed, but in one or two cases it was converted to chloride for weighing :

Digestion of 0.5772 gram of crystals of potassium oxyamidosulphonate for twenty-four hours with a saturated solution of potassium hydroxide and a bit undissolved, still contained a very small quantity of the sulphonic salt undecomposed. But the yield of hyponitrite came up in this case to 76 °/₀. of the full amount ;

Boiling 0.9370 gram of crystals with concentrated potassium hydroxide for a short time was attended with copious effervescence of nitrous oxide, and left still a little undecomposed salt, but the yield of hyponitrite still reached 30 °/₀ of the equivalent of the salt taken.

Merely to prepare hyponitrite from nitrite in this way there is no necessity of getting first a pure oxyamidosulphonate, a well-prepared solution of either alkali-salt sufficiently concentrated is quite serviceable if treated with solid potassium hydroxide. Working in this way we found —

0.4545 gram sodium nitrite,* the final treatment of which, after conversion to the sulphonic salt, was in the cold with the most concentrated potash for twenty-four hours, gave hyponitrite

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* Measured off for analysis as oxyamidosulphonate solution produced from a large quantity of nitrite worked upon.

amounting to 40 °/₀ of the full yield, had all the nitrite been utilised ;

0.5833 gram sodium nitrite,* by final cold treatment for twelve days with the potash, when still a little undecomposed salt remained, gave a yield of hyponitrite equivalent to 33 ½ °/₀ of the nitrite;

0.4171 gram sodium nitrite * by final first cold treatment for twenty-one hours and then at 100° for a quarter-hour yielded hyponitrite amounting to 49 ¾ °/₀ of the calculated quantity.

But in order to get such results as these, referred to the nitrite taken, our modification of the process for getting the oximidosulphonate must be followed, an account of which we reserve for the paper on these salts. Here we need only mention that we can get at least 85 °/₀ of the calculated quantity of oximidosulphonate from nitrite, a proportion far higher than previously got by Raschig, the only quantitative worker.

In consequence of the decomposition of much of the potassium hyponitrite into hydroxide and nitrous oxide, the measure of the hyponitrite does not of itself serve to prove that the formation of this salt is the only decomposition of the oxyamidosulphonate. But it does make this deduction highly probable when taken along with the occurrence of so much nitrous oxide and sulphite, and with no ammonia, nitrogen, or sulphate. The determination of sulphite is, however, what seems sufficient of itself to prove the singleness of the decomposition, although here too any very close approach to the calculated amount cannot be expected, considering the ready oxidisability of sulphites to sulphates, and that not quite all the sulphonate is ever decomposed. In consequence of the presence of hyponitrite and its reaction with iodine, a volumetric estimation of the sulphite with iodine was not possible. We therefore availed ourselves of the

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* See not on p. 221.

reaction of sulphurous acid with stannous chloride for its estimation. Stannous chloride has no action upon hydroxyamine (Divers and Haga, *J. Ch. Soc.* **47**, 624), and none upon oxyamidosulphonic acid.

Our procedure was to put in a pressure-bottle the diluted solution of the salt decomposed by alkali and neutralised, mix it with excess of stannous chloride, and almost fill the bottle with water. Some arsenious oxide was also added in order to fix all hydrogen sulphide in presence of the necessary excess of hot acid, which was, however, not so concentrated as to lead to reduction of arsenic by the tin-solution. The tightly closed bottle was kept in nearly boiling water for an hour, and then left to cool. The washed precipitate of stannous sulphide was heated with hydrochloric acid and potassium chlorate until all sulphur had oxidised, and the solution evaporated to dryness, and again evaporated with hydrochloric acid to dryness. Finally, after removing the tin by hydrogen sulphide, the sulphuric acid in the filtrate was estimated as barium salt. In this way, from 0.7470 gram of salt, which by long keeping had slightly hydrolysed, we got sulphur equivalent to 88.63 per cent. of all in the original sulphonic salt. Another sample, freshly crystallised, in fine plates, was boiled with the potassium hydroxide, entirely out of contact with air, by keeping it in an atmosphere of hydrogen. Thus treated, the product, with the tube containing it, was dropped into the bottle of stannous chloride. In this case, 0.2007 gram gave 89 % (89.05) of the sulphur as sulphite. These results render it clear that sulphite and therefore hyponitrite are the two and only primary products of the change.

The reaction by which hyponitrite and sulphite are formed consists probably in the substitution of the hydrogen of the oxyamido radical by potassium, and then of self-decomposition of the potassium compound. There is no hydrolysis or saponification, simply dissociation or chemical fission—

$$HONHSO_3K + 2KOH = KONKSO_3K + 2H_2O$$
$$2KONKSO_3K = (KON)_2 + 2K_2SO_3$$

Raschig has observed a closely similar decomposition of Fremy's potassium sulphazite by strong potash into sulphite and nitrite.

We would gladly account for the differences between the results found by the other chemists and our own, but we can do little in this direction. We have to face the fact that Claus's work was quantitative. The only suggestion we can offer is that Fremy and Claus's originally pure preparations were not treated with alkali until they had been kept long enough to undergo their usual decomposition (fully in Claus's case)—

$$2HONH(SO_3K),OH_2=(HONH_3)_2SO_4+K_2SO_4$$

into hydroxyamine and sulphate. Such a mixture would behave just as they found. As for oxygen, Fremy must have mistaken nitrous oxide for it, and in making this supposition we have evidently the support of Claus and Raschig. Lastly, as for Claus's nitrous oxide diluted with nitrogen, dilution with air and steam may perhaps have been the cause of his not having got such a gas as Fremy and we ourselves got.

Oxyamidosulphonates evaporated to dryness on a water-bath with either potassium or sodium carbonate evolves carbon dioxide during the last stages of the evaporation, and yields much sulphite. No hyponitrite can remain undecomposed in such circumstances. Even a solution of the oxyamidosulphonate left in the cold for a day with the carbonate shows evidence of the presence of a little sulphite.

Repeated evaporations with potassium acetate leave an alkaline mixture containing a minute quantity of sulphite.

Oxidation of oxyamidosulphonates by basic reagents.

Fremy observed that manganese dioxide dissolved as manganous salt in oxyamidosulphonic acid with effervescence of oxygen. Also that the same reagent caused a lively effervescence in a solution of the potassium salt. In these observations he was right save in mistaking nitrous oxide for oxygen. Finally, he found that the potassium salt immediately reduces salts of silver, copper, and gold. We must except copper from this statement, when alkali is absent Claus found that in the presence of potassium hydroxide the potassium salt reduces salts of copper and silver in the cold, just like hydroxyamine, as we have already had occasion to mention, but he made only qualitative experiments. Raschig, who holds that alkali converts oxyamidosulphonates wholly into their equivalent of hydroxyamine, records no experimental determination of this point, though he quantitatively estimated the hydroxyamine produced by the action of an acid.

The reaction which takes place in our hands is the conversion of the oxyamidosulphonate into sulphite and sulphate and the reduction of a quantity of metal-oxide equivalent to the oxidation of the oxyamide residue, and not of hydroxyamine supposed to be produced. That is to say, the cuprous oxide obtained is half what it would be were hydroxyamine first formed as believed by Claus and Raschig. The equation, therefore, will stand thus —

$$2HONH(SO_3K) + 2CuO + 2KOH =$$
$$K_2SO_3 + K_2SO_4 + Cu_2O + N_2O + 3H_2O$$

which shows the potassium hydroxide taking the two sulphonic residues to form sulphite, sulphate,* and water, and the copper-oxide oxidising to water the one hydrogen of each of the oxyamido residues, thus leaving hyponitrous acid to resolve itself finally into nitrous

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* Hyposulphate was searched for, and could not be found.

oxide and water. After the reduction, addition of hydrochloric acid liberates much sulphur dioxide.

The reaction does not quite complete itself, ceasing when the solutions become very dilute. Thus, if to a solution of one gram of the oxyamidosulphonate in a liter, only a few drops of a dilute solution of copper sulphate and then of potassium hydroxide are added, the mixture shows a permanent blue opalescence, but deposits no cuprous hydroxide, even when preserved for hours in a closed vessel. This observation may serve to show that although, when very dilute, alkali does not produce much sulphite and hyponitrite, this is not because hydroxyamine and sulphate are produced instead, for if such were the case the hydroxyamine would then act upon the cupric hydroxide.

The fact that the alkaline solution contains not hydroxyamine but a sulphonic derivative of it, which gives sulphite in its reactions with reducible bodies, and that it has only half the action of its equivalent of hydroxyamine, are serious, if not fatal, objections to resorting to it as a reagent on organic compounds, as Raschig has suggested may economically be done. This chemist, notwithstanding that he has pointed out (his memoir, p. 182) that the reason that oximidosulphonates do not possess any of the reducing power of hydroxyamine, is that in them the two active hydrogens of hydroxyamine are replaced by sulphonic radicals, and that oxyamidosulphonates by retaining still one of these hydrogens remain as equally easily reducible as hydroxyamine itself, has yet failed to see that, his contention being well-founded, it will be the oxyamidosulphonate and not hydroxyamine which exerts the reducing power of its alkaline solution. That it is so, is shown by the fact, determined by us, that in the absence of reducible agents, alkalis to a small extent do not decompose oxyamidosulphonates and for the rest change them into sulphite and hyponitrite, neither of which gives a cuprous precipitate in presence of alkalis.

We have yet to supply particulars of our quantitative work. The amount of sulphite produced was imperfectly estimated unavoidably, partly because of the great oxidisability of the very dilute alkaline sulphite by air, and partly because of the always incomplete decomposition of the oxyamidosulphonate. To measure it, the mother-liquor of the copper precipitate was run into excess of half-decinormal iodine-solution (mixed with acid enough to more than neutralise the alkali in the mother-liquor), and the unconsumed iodine titrated with sodium thiosulphate. All the water used was previously freed from air by boiling. Of the salt, 1.0967 grams, treated with copper sulphate and potassium hydroxide, gave in this way 40 °/₀ of the sulphur of the salt as sulphite, and that was our best result. Theory, as given by us, indicates 50 °/₀, while on the other view there should be none at all. Other portions of the mother-liquor of the copper precipitate were acidified for hydrolysis of any remaining sulphonate, and concentrated by evaporation. One of these then gave quite a distinct further reduction with the copper mixture, due to hydroxyamine, while another measured portion showed on titration with iodine in presence of potassium-acid-carbonate the presence of hydroxyamine, equivalent however to only one-twelfth of the whole salt.

To measure the amount of copper reduced we added to 0.2913 gram of the salt (already very slightly hydrolysed, by keeping), dissolved in water, a sort of Fehling's solution, much stronger than usual and with much less alkali in it, in slight excess, heated to boiling to collect the cuprous oxide, filtered, rapidly washed, and weighed the reduced oxide as black oxide. We thus obtained cupric oxide equal to 48 °/₀ of the weight of the salt instead of 47 °/₀, calculated from our equation. On the other theory, twice as much should have been got.

We then applied the stannous-chloride process, avoiding all exposure to air by treating the salt in the pressure-bottle to be afterwards used in the analysis, with the alkali and copper salt in a current of hydrogen. To the resulting mixture, and without removal of the cuprous oxide, we added, still in an atmosphere of hydrogen, the necessary stannous-chloride and acid. Only then and for a moment was the bottle opened in order to replace the cork and gas tubes by the stopper of the bottle. Heated, as before, 0.4298 gram of freshly crystallised salt gave 44 % (43.93) of the sulphur as sulphite, a result confirmatory of our theory, and better than that (40 %) got by iodine-titration.

It thus appears clear that the sulphite formed when the oxyamidosulphonate is oxidised by cupric oxide is half what is produced when the salt is decomposed by alkali alone. That only nine-tenths of the reckoned sulphite is obtained in both cases is partly if not entirely due to two causes. One of these is that, as already pointed out, in each mode of decomposition, a little oxyamidosulphonate (or a body like it) is always left at the end of the reaction. The other and main one is that the tin reaction is incomplete, for working upon sulphite of a known degree of purity we have got only 91 and again 93 ½ % of the sulphite indicated.

In alkaline solutions, silver and mercuric hydroxides act quite similarly to cupric hydroxide, qualitatively at least, and yield much sulphite.

Constitution of hyponitrites, as revealed by the decomposition of oxyamidosulphonates.

The decomposition of oxyamidosulphonates into sulphite and hyponitrite sets at rest any doubt as to the constitution of hyponitrites.

For coming in this case directly from a substituted hydroxyamine a hyponitrite must have its oxygen between the nitrogen and metal.

Berthelot and Maquenne have recently published papers (*Compt. rend.* **108**, 1286, 1305) containing analyses of calcium and strontium hyponitrites. These analyses, as they point out, establish the accuracy of the empirical formula given by one of us (Divers) to hyponitrous acid, upon which doubt had been cast by the previous work upon the silver salt by Berthelot himself and Ogier (*Compt. rend.* **96**, 30, 84). To this salt the latter chemists gave the formula $Ag_4N_4O_5$, the correctness of which was afterwards contested by us (*J. Ch. Soc.* **45**, 78). Berthelot now admits this salt to be not obtainable in a pure state, thus also confirming us, as against Zorn, van der Plaats, and Menke, all of whom claimed to have got it pure without difficulty. Zorn's opinion that the molecule of the acid contains two atoms of each of its elements, already generally accepted, is now endorsed by Berthelot and Maquenne. Lastly, Maquenne is disposed to deny that nitrous oxide can be the anhydride of hyponitrous acid, even to the extent that carbon monoxide is the anhydride of formic acid, but on grounds which to us seem quite insufficient. Even the facts recorded in this paper can leave hardly a doubt that it is so. The formula of hyponitrous acid may now confidently be written as HON_2OH or $(NOH)_2$, that is, the acid is hydroximidogen, of which NOH is the radical.