XXX.—*Ammonium Amidosulphite.*

By EDWARD DIVERS and MASATAKA OGAWA.

THE interaction of such familiar gases as ammonia and sulphur dioxide ceased, sixty years ago and more, to attract the attention of investigators, notwithstanding comparatively nothing had then been definitely made out as to the nature of the product, even the few statements concerning it which occur in some of the best treatises on chemistry having but little experimental foundation. The history of the subject is briefly given on p. 331.

Dry Sulphur Dioxide and Ammonia.

Although sulphur dioxide and ammonia, even when comparatively well dried, unite at once and with great energy, yet if sufficient care has been taken to exclude moisture they do not combine. It has not been necessary, however, in order to demonstrate this striking phenomenon, to have resort to the elaborate precautions adopted by Brereton Baker in his well known experiments upon the non-union of hydrogen chloride and ammonia (Trans., 1894, 65, 611; 1898, 73, 422). As sulphur dioxide could be dried better than ammonia, using commercial phosphorus pentoxide for the purpose, we were successful in mixing the gases without their combining only on passing the dioxide first.

The preparation flask, with its tubes, having been heated and then kept for a time in the desiccator, was placed in ice and salt, and a slow current of sulphur dioxide sent through it, the gas having been dried by passing it first through tubes of sulphuric acid and then of phosphorus pentoxide. The outlet-tube dipped into mercury. Ammonia, dried first by cooling in a freezing mixture and then by passing it through long tubes of freshly fused and crushed potassium hydroxide (but no Stas's mixture) was now also passed into the flask slowly. The result was that the interior of the flask remained clear for some minutes, the mixed gases only combining on their escape through the mercury into the air with the production of white fumes of ammonium pyrosulphite; but after a time, the ammonia having, it is presumed, gradually brought in moisture along with it, through passing more rapidly along the tubes than at first, the walls of the flask became suddenly coated with an orange-coloured deposit, whilst the mercury rose high in the exit tube.

Proportions in which Sulphur Dioxide and Ammonia Combine.

The proportions in which ammonia and sulphur dioxide combine, or appear to combine, depend largely on the extent to which the temperature is allowed to rise, the heat of union being considerable. They vary also according as one or other of the gases is in excess, unless the temperature is kept very low. But variation in the proportions, as well as apparent condensation of additional sulphur dioxide by a sufficiently ammoniated product, is clearly due to secondary changes (p. 330). If the temperature is kept low, ammonia unites with sulphur dioxide, especially if the ammonia is in excess, in the proportion of two volumes of the former to one of the latter (p. 330), but since, at the ordinary temperature, this union is immediately followed by a decomposition in which ammonia is evolved, the union of the two gases may appear to take place in other proportions than those just mentioned. It is pretty certain that, by proceeding slowly enough and using strong cooling agents, secondary action can be almost entirely prevented, and the statement just made be verified even when working with the gases alone. We have not striven to make a very close approximation to such a result, because a simple modification of the method enabled us to exclude all secondary action. Our experimental work, which is referred to further on (p. 332), has shown that much more nearly two volumes than one volume of ammonia can be made in this way to unite with one volume of sulphur dioxide, the only proportions which Rose met with in his experiments (p. 332), and that the presence of much ammonium amidosulphite in the product can be established with certainty.

Preparation and Analysis of Ammonium Amidosulphite.

In order to get the primary product of the union of sulphur dioxide with ammonia in an unchanged state, ether was made use of. The ether, freed from alcohol and water by treatment with sodium, was contained in a small flask, fitted with inlet and outlet tubes, which was to serve, not only for the production of the new substance, but for its isolation and its weighing for analysis. The flask was put in a bath of ice and salt, with the outlet tube dipping into a trough of mercury, and the ether was saturated with dried ammonia; having shut off the ammonia, a very slow current of sulphur dioxide was then sent into the solution while the flask was continuously shaken, not only in order to diffuse the heat, but to prevent the product from caking on to the bottom of the flask and enclosing ether. The mouth of the tube containing the sulphur dioxide soon became filled with a yellow, pasty mass (p. 330), and had to be kept open by a platinum rod, manipulated through the rubber tubing above, but the precipitate itself was quite white and powdery. In spite of the external cooling, the heat of combining was sufficient to cause ammonia gas, saturated with ether vapour, to escape through the mercury sealing the exit tube, and when this escape became slight, the passage of sulphur dioxide was stopped. Using about 20 c.c. of ether, more than a gram of the substance was obtained. In order to secure this undecomposed, a second flask was put in connection with the preparation flask, and ammonia again passed to the saturation point. The ammoniated ether was decanted off through the connecting tube into the second flask, which was then detached, and the ether adhering to the precipitate was removed by passing a current of ammonia over the precipitate in the flask for some hours, the whole operation being carried out in the freezing mixture. There was no other means of completely drying the salt, and even this was not altogether successful if the salt had been allowed to cake together. Neither air nor hydrogen could be used in place of ammonia for drying the salt, nor could the flask remain out of the freezing mixture so long as ether still moistened the salt, without the latter acquiring an orange colour. When dry and in an ammoniacal atmosphere, the salt is more stable, but cannot long be kept at the ordinary temperature without becoming discoloured through decomposition.

Analysis.—The stopper carrying the gas tubes having been replaced by a plain one, and air allowed to displace most of the ammonia gas, the flask was at once weighed and left for a time inverted with the open mouth dipping into 100 c.c., or more, of water in a beaker. When the salt in it had become damp, it was washed into the water, and its very dilute solution distilled with alkali to determine the ammonia.

330 DIVERS AND OGAWA: AMMONIUM AMIDOSULPHITE.

The residue was divided into two measured portions, one of which was acidified and heated at 150° under pressure for some hours, and then redistilled with alkali for additional ammonia, of which only a trace was obtained (0.001 per cent. of the salt). The other part of the solution was treated with bromine, and next with hydrochloric acid and potassium chlorate, after which the sulphuric acid was precipitated as barium sulphate with the usual precautions. The results of the analysis were :

	Ammonia.	Sulphur dioxide.
Found	35.09 ;	64.91 per cent.
$\text{SO}_2(\text{NH}_3)_2$ requires	34.69 ;	65.31 ,,

The slight excess of ammonia indicated may safely be attributed to the means taken to preserve the salt until it was analysed.

Its Properties, Constitution, and Name.

The new salt, which is white and apparently crystalline, seems to be slightly volatile in a current of ammonia. It is very deliquescent, and, on exposure to the air, decomposes, losing ammonia. It dissolves in water, giving out heat and a hissing sound, and if dissolved by ice or enough ice-cold water, furnishes a solution answering all the tests for pure ammonium sulphite. In this respect, it is quite unlike ammonium amidosulphate or carbamate, since even the latter salt gives at first no precipitate with calcium chloride, which at once precipitates all sulphite from the new salt. When the salt is much decomposed, its solution gives other reactions besides those of a sulphite. In anhydrous alcohol, it dissolves freely, evidently as ethyl ammoniumsulphite ; it is also slightly soluble in dry ether. It soon begins to change, and then assumes an orange colour, even at the common temperature. At $30\text{--}35^{\circ}$, it decomposes into a liquid and a solid part, both more or less orange-coloured, and into ammonia, the liquid part undergoing further change into solid matters (p. 333).

Constitution.—The salt is more probably an amido- than an imido-compound, $\text{NH}_4\cdot\text{N}(\text{SO}_2\cdot\text{NH}_3)_2$ (analogue of normal ammonium imidosulphate), because it can be obtained only when the temperature is kept low and the ammonia is in excess. It is still more probably a sulphuryl rather than a thionyl compound, because of its feeble activity as a reducing agent, and of its very easy passage into ammonium sulphite or ethyl ammoniumsulphite. It has accordingly to be formulated as $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}_4$, and not as $\text{NH}_2\cdot\text{SO}\cdot\text{ONH}_4$.

Name.—Since the salt represents ammonium sulphite, $\text{NH}_4\text{O}\cdot\text{SO}_2\cdot\text{NH}_4$, in which the ammonoxyl is replaced by amidogen, it is properly called ammonium amidosulphite. Berglund's name of amidosulphonate, now in use for amidosulphate, is evidently based on a misconception.

The name, amidosulphinate, in analogy with amidosulphonate, must be rejected on the same grounds, and because the salt has not the characteristic reducing action and the constitution of sulphinates. It does not seem possible, even were it desirable, to construct a term for the first amide of sulphurous acid that would correspond with sulphamic acid, the synonym of amidosulphuric acid.

Nature of the Decomposition which the Amidosulphite undergoes when Heated.

History.—Experiments on the union of sulphur dioxide with ammonia made earlier than ours gave the products of decomposition of ammonium amidosulphite instead of the salt itself. Döbereiner, in 1826 (*Schw. Jahrb.*, 17, 120), described the product of the union as a brownish-yellow vapour which quickly condenses to a bright brown, solid mass, 'anhydrous ammonium sulphite,' which the smallest quantity of water converts into ammonium sulphite. Rose published three papers on "anhydrous sulphite of ammonia" in 1834, 1837, and 1844 (*Pogg. Ann.*, 33, 235; 42, 415; 61, 397), in the second correcting statements made in the first, and modifying, in the third, the views he had expressed in the earlier papers. The outcome was that he had ascertained that the product of the union is always one and the same single substance, in whatever proportions the dry gases are taken; that it is composed of equal volumes of the gases, is either yellowish-red and viscid, or red and crystalline, very deliquescent, and dissolves very easily in water without evolving ammonia; that it yields a neutral solution, which is at first yellowish, but soon becomes colourless, and gives, when recently prepared, the reactions mainly of a mixture of ammonium sulphate and trithionate, but to a small extent those of a sulphite also; and, lastly, that when the solution is of a certain concentration it gives a transient, reddish coloration with hydrochloric acid.

Forchhammer (*Compt. rend.*, 1837, 5, 395) found that, besides the orange-coloured substance, crystals of ammonium sulphate are produced, which can sometimes be seen apart from the other product in some spots of the mass, although often indistinguishably mixed up with it. (That the crystals observed in the product were those of sulphate could only have been a supposition of Forchhammer's.) The mass, when moistened, is alkaline, and evolves ammonia, yielding, in other respects, the reactions recorded by Rose. Absolute alcohol extracts from it a substance which acquires a rose colour, soon disappearing. Indirectly, he represented the mass to be derived from 2 mols. of ammonia to 1 mol. of sulphur dioxide.

The views advanced as to the nature of the orange-coloured sub-

stance have been, that it is a compound of ammonia with an isomeride of sulphurous anhydride, which, with water, changes at once into ammonium sulphate and trithionate, just as ammonium pyrosulphite slowly changes in hot solution (Rose); that it is amidogen sulphide, $S(NH_2)_2$, mixed with ammonium sulphate (Forchhammer); that it is partly thionamic acid, $NH_2 \cdot SO \cdot OH$, partly ammonium thionamate, both volatile, its colour being due to an impurity (H. Watts); and that it is ammonium pyrothionamate, $NH_2 \cdot S_2O_4 \cdot NH_4$ (Jörgenssen).

Interaction of the Gases.—We have repeated Rose's experiments of measuring over mercury the volumes of the gases which interact, he having found that combination always takes place between equal volumes, whichever gas is in excess. The results somewhat approached this when no steps were taken to prevent the rise in temperature due to the union of the gases; but when the gas tube was immersed in a cooling mixture and the ammonia was in excess, the volume of this gas consumed was much greater than that of the sulphur dioxide. This method of investigating the matter is, however, inapplicable, because the ammonium amidosulphite which is formed partly decomposes and evolves ammonia freely. By letting the dried gases come together in a vessel agitated in a freezing mixture, and keeping the ammonia in excess, a solid mass is obtained which consists largely of the amidosulphite, and behaves as such with water, although it is mixed with other substances, quantitative analysis showing that much more than 3 mols. of ammonia to 2 mols. of sulphur dioxide are required for its formation. If, instead of being examined at once, it is kept for a long time in a gentle current of dry nitrogen or hydrogen at a temperature of $30-35^\circ$, it no longer contains amidosulphite or gives any sulphite to water, and contains not much more than one atom of nitrogen to one of sulphur. Thus, Rose's results are explained, and, at the same time, shown to be of no direct significance.

Products of the Decomposition.—Both Rose and Forchhammer found ammonium sulphate to be a principal constituent of the product of the interaction of the gases. If the temperature had risen sufficiently high, this would have been the case; furthermore, the solution of the even less heated product slowly becomes acid and full of sulphate. When, however, the temperature has not been allowed to exceed 30° , or even 40° , the quantity of sulphate in the product is so small that it may almost be disregarded. Together with the sulphate, trithionate was considered by Rose to make up most of the product, for the aqueous solution of the mass always gives a strong reaction with silver nitrate which might be that of trithionate; moreover, in the case of his product, other reactions of a trithionate were noticed. When, however, the product has been carefully prepared and is free from amidosulphite, its solution gives the silver reaction without the others which belong to a

trithionate. For instance, the solution may be acidified and left for hours without yielding more than mere traces of sulphur dioxide and sulphur; to get these in quantity, the solution has to be strongly heated under pressure. Besides this, the absence of sulphate in the solution is of itself almost enough to disprove the production of trithionate, since, as Rose himself held, sulphate and trithionate as products of the decomposition are complementary.

Pure ammonium amidosulphite, when heated, gives the same results as the coloured product obtained by the union of sulphur dioxide and ammonia.

Rose's assertion that the product formed by the union of the gases is homogeneous is certainly incorrect, according to our experience. By the union of the gases in a receiver kept well cooled, the product is deposited as a soft, waxy, yellow coating on the walls of the vessel and on the gas-tubes. Its colour varies in different parts from nearly white to orange-red, somewhat irregularly, but generally so as to be whiter near where the ammonia enters, the whiteness not being due to moisture in the gases, as Rose assumed. When the temperature rises to 30—35°, whether by the heat of reaction or by external heat, it is decomposed into an indistinctly crystalline, white solid, and a much smaller quantity of a coloured, effervescing liquid, partly draining to the bottom of the vessel; after a time, however, the whole becomes solid again, and adheres tenaciously to the glass. When pure ammonium amidosulphite is similarly heated in a dry, inactive gas, it becomes coloured, softens, sinters together, vesiculates, gives off ammonia, and becomes a mass like that derived directly from the union of the gases. With very gradual heating, the temporarily liquid product is much less coloured than in the other case, its colour being evidently caused by the presence of a red matter dissolved in it, which gives indications of being volatile.

This orange-red substance is never formed except in very small quantity. It gives a yellow colour to the aqueous solution of the whole product, which, however, slowly fades. Alcohol, carbon disulphide, and other menstrua dissolve it out from the salts, leaving them white; but the solutions are not pure. The yellow solution in water or alcohol takes a transient pink colour when mixed with dilute hydrochloric acid, and the alcoholic solution, an indigo-blue colour with concentrated ammonia. The residue left on evaporating the carbon disulphide solution becomes explosive when heated above 150°, and may then have become nitrogen sulphide, but before being heated it is not this substance.

Except the very little sulphate already mentioned, there is no known substance present in the residue of the decomposition of the amidosulphite by a gentle heat, so far as we can discover. Alcohol of

95 per cent. dissolves out something, but only very sparingly ; on evaporating the solution in a vacuum, a very deliquescent salt is obtained in crystals, having a composition which may be expressed by $9\text{NH}_3, 8\text{SO}_2$, assuming the presence of 2.5 per cent. moisture. The composition of the whole crude residue does not differ much from this. The alcoholic solution, if cooled and saturated with ammonia, gives minute, scaly crystals in small quantity. This substance, dried in a current of ammonia, has a composition expressed by the formula $(\text{NH}_3)_3\text{S}_2\text{O}_3$, and if dried over sulphuric acid, that of $(\text{NH}_3)_2\text{S}_2\text{O}_3$. These three substances all give the silver nitrate reaction of the aqueous solution of the whole residue, and when boiled with dilute hydrochloric acid give very little sulphur and no sulphur dioxide. At higher temperatures, whether dry or in solution, they yield sulphur, sulphur dioxide, and sulphate. Two potassium derivatives of these salts have also been prepared. Neither the crude residue nor any of the above substances yields all its nitrogen as ammonia when distilled with alkali, unless it has been previously heated with hydrochloric acid under pressure.

From the mother liquor of the above-mentioned S_2O_3 salt, a substance was obtained which in composition and behaviour appeared to be sulphamide, slightly impure. Neither sulphamide nor amidosulphate can be found in the fresh aqueous solution of the whole residue, but, by heating the solid residue itself to a higher temperature, imidosulphate is obtained in considerable quantity, besides sulphur and sulphate, and imidosulphate is known to be a product formed when either amidosulphate or sulphamide is first heated, and then dissolved in water. An extract from the residue made with proof-spirit or with wood spirit yields ammonium amidosulphate on evaporation, no doubt generated by hydration. When an aqueous solution of the heated residue was treated with excess of barium acetate, filtered, and evaporated at 100° , it left crystals of barium thiosulphate.

During the heating of ammonium amidosulphite at a temperature of 30° to 35° , besides much ammonia, small quantities of water and of sulphur dioxide are evolved, the former mainly in the earlier stage and the latter in the later stage of the decomposition. This remarkable production of water, although always evident, was fully established by cooling the escaping gases and testing the water thus collected. The presence of sulphur dioxide later in the operation was shown by the gases fuming on their escape into the air, and then forming a small, white deposit, slowly turning orange, and reacting as ammonium pyrosulphite. In the interaction of sulphur dioxide with ammonia, and in the decomposition of the amidosulphite, no liberation of nitrogen could ever be discovered.

To sum up the results of our incomplete work on the decomposition

of ammonium amidosulphite by a graduated and gentle heat: ammonia and a residue consisting of a substance (or substances) which behaves as a thio-amido-sulphonic compound are the principal products; in far smaller quantities, water and an orange-red substance are also produced, and generally, if not always, a very little sulphate; whilst as secondary products, apparently sulphamide and certainly amidosulphate and thiosulphate are obtainable, as well as imidosulphate, sulphur, and much sulphate. It seems of interest to point out that we here record the first production known of amidosulphate from ammonia and sulphur dioxide, this, hitherto, having been derived either from ammonia and sulphur trioxide, or from a nitrite and sulphur dioxide.

We hope in a future paper to be able to report the completion of this investigation.