

## **Ammonium Amidosulphite.**

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The interaction of such familiar gases as ammonia and sulphur dioxide ceased to attract with any effect the attention of investigators sixty years ago and more. Yet comparatively nothing had then been definitely made out about the nature of the product, and even the few statements concerning it in some of the best treatises on chemistry have but little experimental foundation. The history of the subject is briefly given on p. 193.

### *Non-union of dry sulphur dioxide and ammonia.*

Even when comparatively well-dried, sulphur dioxide and ammonia unite at once and with great energy when brought together; yet they can remain mixed without combining, provided sufficient care has been observed to exclude moisture. 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 famous experiments upon the non-union of hydrochloric acid and ammonia (*J. Ch. Soc.*, 1894, 65, 611; 1898, 73, 422), and we have only dried the gases during their flow through the tubes. As we were able to dry sulphur dioxide better than ammonia, because common phosphorus pentoxide could be used for the purpose, we have had success in mixing the gases without their combining only by giving this gas precedence. The preparation flask with its tubes having been heated and then kept for a while in the desiccator, was placed in ice and salt while a slow current was sent through it of sulphur dioxide, which had passed through drying-tubes of sulphuric acid and then of phosphorus pentoxide. The outlet-tube dipped into mercury. Ammonia, dried first by the cold of a freezing-mixture and then by 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. But the ammonia having, it is presumed, gradually brought enough moisture 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, while 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 together, depend largely upon 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 used in excess, unless the temperature is kept very low. But the variation of the proportions and the apparent condensation of additional sulphur dioxide by a sufficiently ammoniated product, that may be observed, are results clearly due to the secondary changes going on (p. 192). The simple union of ammonia and sulphur dioxide, which can be secured by keeping down the temperature by suitable means, especially with the ammonia in excess, is that of two volumes of the former to one of the latter (p. 191). But since this union cannot be made at the ordinary temperature without being immediately followed by a decomposition, in which ammonia is evolved, the union of the two gases can appear to take place in other proportions than the above. It is pretty certain that, by proceeding slowly enough and using strong cooling agencies, secondary action could be almost entirely prevented and the statement just made be verified, even when working with the gases alone. We have not gone very near to getting such a result in this way, but then we have, for good reasons, not striven much to overcome the difficulties. Our experimental work, which will be further on referred to (p. 195), has shown that two much more nearly 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. 193), 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 its unchanged state, ether was

made use of as the medium of the union, in order to keep the temperature under control. The ether, freed from alcohol and water by 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 then the ether was saturated with dried ammonia. Having shut off the ammonia, a very slow current of sulphur dioxide was 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 shutting in ether. The mouth of the tube conveying the sulphur dioxide soon became filled with a yellow pasty mass (p. 192), 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 stopped. With the use of about 20 c.c. ether, there had then formed well over a gram of the substance. 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, the whole operation being carried out in the freezing-mixture. The current of ammonia was renewed over the precipitate in the flask, and continued for hours, until all the ether adhering to the precipitate had been carried away, the flask being all the while still

in the freezing-mixture. There was no other way of completely drying the salt, and even this way was not sufficiently successful when the salt had been allowed to cake together. The ammonia could not be replaced by air or hydrogen for drying the salt, nor could the flask be kept out of the freezing-mixture, so long as ether still moistened the salt, without the latter taking an orange-colour. When dry and in an ammonical atmosphere, the salt is more stable, but cannot long be kept at the ordinary temperature without getting 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 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 for its ammonia. The residue was divided into two measured portions, one of which was acidified and heated to 150° under pressure for some hours and then redistilled with alkali for additional ammonia, of which only a trace was got (0.001 per cent. of the salt). The other part of the solution was treated with bromine, and next with hydrochloric acid and chlorate, after which barium sulphate was precipitated with the usual precautions. The results of the analysis were:—

	Ammonia	Sulphur diox.
Found:	35.09;	64.91 per cent.
SO <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> :	34.69;	65.31 „

The slight excess of ammonia indicated is safely attributable to the means taken to preserve the salt till it was analysed.

*Its properties, constitution, and name.*

The new salt is white and apparently crystalline, and appears to be slightly volatile in a current of ammonia. It is very deliquescent and decomposes, losing ammonia, in the air. 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 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 30-35° 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. 197)

*Constitution.*—The salt is more probably an amido- than an imido-compound,  $\text{NH}_4\text{N}(\text{SO}_2\text{NH}_4)_2$  (analogue of normal ammonium imidosulphate), because it can be obtained only when the temperature is kept down 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  $\text{NH}_2\cdot\text{SO}\cdot\text{ONH}_4$ .

*Name.*—Since the salt represents ammonium sulphite,  $\text{NH}_4\cdot\text{SO}_2\cdot\text{NH}_4$ , in which the ammonoxyl is replaced by amido-

gen, 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 to that of sulphamic acid, the synonym of amidosulphuric acid.

*Nature of the decomposition by heat of the amidosulphite.*

*History.*—Experiments made earlier than ours on the union of sulphur dioxide with ammonia gave the products of decomposition of ammonium amidosulphite instead of the salt itself. Doebereiner in 1826 (*Schw. Jahrb.*, 17, 120), described the product of the union as a brown-yellow vapour quickly condensing to a bright brown solid mass, which the smallest quantity of water converts into (colourless) 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 smeary, or red crystalline, very deliquescent and very soluble 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 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 by the union of the gases, which can sometimes be seen apart from the other product in some spots of the mass, though 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 otherwise the reactions recorded by Rose. Absolute alcohol dissolves out of it a substance which takes a rose colour, soon disappearing. Indirectly, he represented the mass to be derived from two mols. ammonia to one mol. sulphur dioxide, as did also Doebrenier.

The views advanced as to the nature of the orange body have been, that it is a compound of ammonia with an isomer of sulphurous anhydride, which changes at once with water 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, being its colour due to impurity (H. Watts) ; and that it is ammonium pyrothionamate,  $NH_2 \cdot S_2O_4 \cdot NH_4$  (Joergensen).

*Interaction of the gases.*—We have repeated Rose's experiments of measuring over mercury the volumes of the gases which



interact, in which he found that always equal volumes combine, whichever gas may be taken in excess. The results somewhat approached this when no steps were taken to restrain 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 with free evolution of ammonia. 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, behaving as such in water, though mixed with other substances, and quantitative analysis of which shows that much more than three mols. ammonia to two mols. sulphur dioxide have gone to its formation. If, instead of examining it at once, it is kept for a long time in a gentle current of dry nitrogen or hydrogen, at a temperature of  $30^{\circ}$  to  $35^{\circ}$ , 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. A sufficiently high temperature having been reached, this will have been the case; furthermore, the solution of the even less heated product slowly becomes acid and full of sulphate. But when the temperature has not been allowed to exceed  $30^{\circ}$ , or even  $40^{\circ}$ , the quantity of sulphate in the product is so small that it may almost be dis-

regarded. Along with 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 and, in the case of his product, gave other reactions of a trithionate. But when the product has been carefully prepared and is free from amidosulphite, its solution gives the silver reaction without the others belonging to a trithionate. Thus, 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 had 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 represented, sulphate and trithionate are complementary products of the decomposition.

Heating pure ammonium amidosulphite gives the same results as heating the coloured product of the union of sulphur dioxide and ammonia as gases. Rose's assertion that the product is a single substance, even in appearance, 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 product gets to 30-35°, whether by its own heating or by external heat, it is decomposed at first into an obscurely crystalline white solid and a much smaller quantity of a coloured, effervescing liquid, partly draining to the bottom of the vessel; after a time all becomes

solid again and tenaciously adherent to the glass. When pure ammonium amidosulphite is similarly heated in a dry inactive gas, it colours, softens, shrinks together, vesiculates, gives out 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 in more than very small quantity. It gives a yellow colour to the aqueous solution of the whole product, which, however, slowly fades away. Alcohol, carbon bisulphide, 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-bisulphide-solution becomes explosive when heated above  $150^{\circ}$ , 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 as-yet known substance present in the residue of the decomposition of the amidosulphite by a gentle heat, so far as we can discover. Alcohol of 90 per cent. dissolves out something, but only very sparingly. By evaporation of the solution in a vacuum desiccator, a very deliquescent salt is obtained in crystals, having a composition that 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 alco-

holic solution, cooled and charged with ammonia, gives minute scaly crystals in small quantity. This substance, dried in a current of ammonia, has a composition expressed by  $(\text{NH}_3)_3\text{S}_2\text{O}_3$ , and dried in the sulphuric-acid desiccator, 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 on boiling 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 first heated with hydrochloric acid under pressure.

From the mother-liquor of the above mentioned  $\text{S}_2\text{O}_3$  salt a substance was got which in composition and behaviour appeared to be sulphamide a little 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 a known product of first heating and then dissolving in water, either amidosulphate or sulphamide. A proof-spirit extract and also a wood-spirit extract of the residue yield ammonium amidosulphate on evaporation, no doubt generated by hydration. An aqueous solution of the less heated residue, treated with excess of barium acetate and filtered, gave barium thiosulphate in crystals, on evaporating it over the water-bath.

During the heating of ammonium amidosulphite at a temperature of  $30^\circ$  to  $35^\circ$ , besides much ammonia, small quantities of water and of sulphur dioxide are evolved, the former mainly

in the early stage and the latter in the late stage of the decomposition. This remarkable production of water, though 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 upon 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 much less quantities, water and an orange-red substance are also produced, and, generally if not always, a very little sulphate; and, 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, which, hitherto, has 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.

