

## Ammonium and other Imidosulphites.

By

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The fact of the existence of ammonium imidosulphite as a product of the decomposition of the amidosulphite by very gentle heating,



was brought before a meeting of the London Chemical Society last session (*Proc. Chem. Soc.* 1900, 16, 113). The present paper consists of a fuller account of this salt and other imidosulphites than could then be given.

Ammonium amidosulphite, from which the imide salt is derived (this Journal, 1900, 13, 187), is readily formed by the union of sulphur dioxide and ammonia, but is so unstable as to be largely decomposed by the unavoidable heating it suffers when these gases come together, unless cooled ether be used as their solvent. On keeping the dry salt at a temperature of about 35°, its decomposition goes on and ammonia escapes for some hours.

There is left a mottled orange mass, of waxy consistence, already described in the earlier paper (*loc. cit.*, p. 196), which is difficult to attack with solvents other than water, because it adheres very firmly to the vessel and must not be exposed to the air during treatment. By protracted digestion with successive portions of 90 per cent. spirit, aided by scraping with a pointed glass rod and strong shaking, it can however be nearly all dissolved up although only very sparingly soluble. The first portions of the solution are coloured and contain a salt the presence of which interferes with the preparation of the imidosulphite from them. The later colourless extracts yield the imidosulphite when they are evaporated, in the vacuum desiccator but not quite pure. Much better results are got by beginning the treatment with warm 95 per cent. spirit, used in successive portions, until the residue is a colourless powder, and only then resorting to the 90 per cent. spirit and carrying on the digestion at about 50°. The solution thus obtained deposits almost pure imidosulphite as it cools, and the mother-liquor can be used with advantage again and again to dissolve out more of the salt, although in that case the crystals which separate are somewhat impure. These can be purified by washing with absolute alcohol containing much ammonia to dissolve out the foreign salt (more soluble in presence of ammonia), and then dissolving up in warm 90 per cent. spirit and recrystallising. The original mother-liquor yields more imidosulphite, but impure, when it is either artificially cooled (as by ice and salt), or is evaporated in the desiccator. This impure salt can be purified in the way just described. All the ammonium imidosulphite is finally washed with ammoniacal alcohol, drained on a porous tile under close cover, and dried in a potash-desiccator. The quantity of pure salt actually obtained in this way approaches

that of a fourth only of the weight of decomposed amidosulphite taken, but the total production of imidosulphite will no doubt prove to be very much greater.

*Analysis.*—The salt, 0.4240 gram, distilled with potash yielded ammonia, 0.0817 gram, and then after heating for some time in a pressure-tube with hydrochloric acid and again distilling with potash, 0.03755 gram more ammonia. Simple distillation with potash of 0.4912 gram of another portion of salt gave 0.0939 gram of ammonia, and then, after oxidation by means of bromine followed by hydrochloric acid and potassium chlorate, 1.2886 grams of barium sulphate. The calculated and found percentages are :—

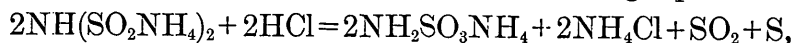
	Ammonia nitrogen.	Imide nitrogen.	Total nitrogen.	Sulphur.
$\text{NH}(\text{SO}_2\text{NH}_4)_2$ ;	15.64	7.82	23.46	35.75
Found ;	15.86	7.29	23.15	—
„	15.74	—	—	36.02

It will be seen that the analysis establishes not only the composition of the salt to be  $3\text{NH}_3, 2\text{SO}_2$  but also its imide constitution.

*Properties.*—It occurs in minute micaceous needles. Heated very slowly in a tube it soon begins to decompose into volatile substances and a residue of sulphur, ammonium sulphate, and the  $\frac{2}{3}$  normal ammonium imidosulphate  $[\text{NH}(\text{SO}_3\text{NH}_4)_2]$ . Even when the temperature is raised to  $150^\circ$ , no fusion takes place. The sublimates which form during the heating begin to appear at about  $80^\circ$  and consist apparently of ammonium pyrosulphite  $[(\text{NH}_4)_2\text{S}_2\text{O}_5]$ , and the unchanged imidosulphite  $[(\text{NH}_4)_2\text{S}_2\text{O}_4\text{NH}]$ . The salt is insoluble in alcohol, and in this respect is unlike ammonium amidosulphite, which is very soluble as ethyl ammonium-

sulphite and ammonia. The salt is only moderately deliquescent and, freshly prepared, is neutral to litmus.\* It has a mild, unpleasant, sulphurous taste, which distinguishes it from the salt occurring with it, more freely soluble than it in 95 per cent. spirit, and already referred to.

It is freely soluble in water but slowly decomposes into thiosulphate and amidosulphate. This change beginning at once, the solution gives all the reactions of a thiosulphate. It goes on also in presence of hydrochloric acid, which when hot hastens its completion. Barium thiosulphate has been prepared from the solution, and amidosulphuric acid and ammonium amidosulphate also obtained from it. Quantitative determinations of the sulphur, sulphur dioxide, and amidosulphate, formed on boiling with hydrochloric acid, gave results in agreement with the following equation:—



in which the  $\text{SO}_2$  and S represent decomposed thiosulphuric anhydride.

*Potassium imidosulphite*.—It has already been stated when detailing the analysis of the ammonium salt that that salt yields just two-thirds of its nitrogen as ammonia when boiled with potassium hydroxide in aqueous solution. In accordance with this fact, it has been found that potassium imidosulphite is obtained when to the ammonium salt dissolved in 70 per cent. spirit, alcoholic potash is added until the solution just renders red litmus paper permanently blue on exposure to air. The salt soon separates as minute micaceous crystals firmly adherent to the glass. After

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\* As first obtained by us last year and then described, the salt had an acid reaction and was exceedingly deliquescent. But as it showed a deficiency in ammonia (22.2 instead of 23.5 per cent.), and as its potassium derivative was not acid, we indicated our expectation that when obtained in a purer state the salt would prove to differ somewhat in properties from what we had then found.

repeated washing with absolute alcohol, the salt has been found to remain alkaline to litmus, quite possibly, however, because of the presence of a trace of tripotassium salt, as happens in the case of imidosulphates. The imidosulphite, unlike the corresponding potassium imidosulphate  $\text{NH}(\text{SO}_3\text{K})_2$ , is very soluble in water and its solution gives the imidosulphite reactions of the ammonium salt. It has too the sulphurous taste of that salt. In the analysis, nitrogen was determined by the combustion method, sulphur by oxidation as in the analysis of the ammonium salt, and potassium by ignition with sulphuric acid, with the following results:—

	Pottasium.	Nitrogen.	Sulphur.
$\text{NH}(\text{SO}_2\text{K})_2$ ;	35.29	6.33	28.96
Found ;	35.17	6.74	28.88
„	—	6.93	—

*Barium ammonium imidosulphite.*—When the orange mass of decomposed amidosulphite is dissolved in water and mixed with baryta water in such quantity as to leave undecomposed some of the ammonium imidosulphite it contains, the filtered solution when concentrated in the desiccator deposits the double salt in minute micaceous crystals. Only barium and sulphur were determined. The results agree with calculation for  $\text{Ba}(\text{SO}_2\text{NHSO}_2\text{NH}_4)_2$ .

	Barium.	Sulphur.
$\text{BaN}_4\text{H}_{10}\text{S}_4\text{O}_8$ ;	29.85	27.89
Found ;	29.94	26.90

In the *Proc. Chem. Soc.*, (1900, 16, 104), the existence of this salt was indicated, but by mistake it had been taken to be a salt of the acid,  $\text{N}_2\text{H}_4\text{S}_2\text{O}_3$ , and was accordingly formulated as

$\text{Ba}(\text{N}_2\text{H}_3\text{S}_2\text{O}_3)_2, 2\text{OH}_2$ . It is soluble in water and its solution behaves as that of an imidosulphite, being precipitable by baryta ( $\text{N}_2\text{H}_4\text{S}_2\text{O}_3$  salts are not), and besides at once gives off ammonia when moistened with potassium or barium hydroxide solution.

The treatment of the orange mass of decomposed ammonium amidosulphite with 95 per cent. spirit, as a preliminary to dissolving out the main quantity of imidosulphite with 90 per cent. spirit, yields yellow alcoholic solutions which on evaporation in the desiccator deposit crystals which are short thick prisms almost cubical in appearance and about 2 mm. across. They are thus quite unlike the minute micaceous needles of ammonium imidosulphite. They are yellow but the colour is adventitious. They can be purified and rendered white by putting them into 95 per cent. spirit and then almost saturating this with ammonia while the containing flask is kept immersed in cold water. In this alcoholic ammonia they are very sensibly soluble. The solution is decanted and the treatment repeated until only a small quantity of white powdery salt remains, principally imidosulphite. The solutions left for a while in open flasks and then exposed in the desiccator over sulphuric acid lose most of the ammonia, and the crystals reform from the solution. Washed with alcohol they are left quite colourless. The mother-liquors evaporated in the desiccator yield crude yellow crystals again which can be recrystallised from alcoholic ammonia as before.

These crystals are recrystallisable without change and have also been prepared by us in two successive winters, yet they give analytical results which are closely concordant with the remarkable empirical formula,  $4\text{NH}_3, 5\text{SO}_2$  or  $\text{N}_4\text{H}_{12}\text{S}_5\text{O}_{10}$ .

	Nitrogen.	Sulphur.
$N_4H_{12}S_5O_{10}$ ;	14.43	41.24
Found in 1900 ;	14.11	41.14
” ”	14.36	40.82
” in 1901 ;	14.02	41.02
” ”	14.40	—

These crystals are neutral and have a bitter taste, not a sulphurous one. They are freely soluble in water and very deliquescent. The solution is unstable and in some of its reactions greatly resembles that of ammonium imidosulphite. With potassium hydroxide the salt evolves ammonia at once, but analysis of potassium salts prepared from it in 70 per cent. alcoholic solution have given discordant results. A striking difference from an imidosulphite is that its fresh solution gives no barium precipitate even in presence of ammonia. Also that in freshly prepared solution, it does not decolourise iodine solution, and only slowly cold acid permanganate. It also does not give the ferric-chloride colouration of a thiosulphate which the imidosulphite does give. Its solution becomes very acid after a time and then smells much more strongly of sulphur dioxide than a similar solution of imidosulphite. The crystalline matter having nearly the composition expressed by  $9NH_3, 8SO_2$ , mentioned on p. 197 of our paper on ammonium amidosulphite (this Journal, 1900, 13), we believe to have been the present salt mixed with imidosulphite and amidosulphate. On a future occasion we hope to be in a position to report upon the constitution of the body we have here described.

