

## Preparation of Sulphamide from Ammonium Amidosulphite.

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Sulphamide occurs among the products of the spontaneous decomposition of ammonium amidosulphite. That this appeared to be the case was mentioned in the paper describing this salt (this Journal, 1900, **18**, 187). It had then been isolated not only in too small a quantity to admit of its purification and full analysis, but in a way that rendered its identity almost doubtful. The decomposed amidosulphite had been extracted with 95 per cent. alcohol, the residue from the evaporated voluminous solution extracted with undried ether, and the again very voluminous solution evaporated. Half a gram of crystalline residue from about 150 c. c. of the ether solution was thus obtained, answering the tests for sulphamide, but melting much above  $81^{\circ}$ , tasting not bitter, and yielding a little too much sulphur on analysis. Then, too, we had failed to get silver sulphamide from the aqueous solution of the decomposed amidosulphite, owing, as we afterwards found, to our having used ammonia in excess. All these points differed, or seemed to differ, from TRAUBE's description, and caused us to hesitate in pronouncing the substance to be sulphamide. Since then, we have obtained it in larger quantity and pure, and

thus become certain that sulphamide is a little soluble in absolute alcohol and even very slightly so in dry ether, that it melts at  $91^{\circ}$ , and that its silver derivative is insoluble in ammonia alone, but soluble in ammonia in presence of the ammonium nitrate which its mother-liquor always contains. The publication of HANTZSCH and HOLL's important contribution to the knowledge of sulphimide and sulphamide (*Ber.*, 1901, **34**, 30), in which TRAUBE's account of sulphamide (*Ber.*, 1893, **26**, 609) is amended, affords welcome confirmation, so far as it goes, of the correctness of our own observations.

Hitherto, as well is known, sulphamide has only been got from sulphuryl chloride and ammonia, a mode of preparing it which HANTZSCH and HOLL have shown to be most laborious and unprofitable, and the difficulty of getting it in this way has quite recently induced Ephraim to try to obtain it from sulphuryl chloride by means of urethane, but without success (*Ber.*, 1902, **35**, 776). Sulphuryl chloride is stated to give only 1–2 per cent. of pure sulphamide, whilst ammonium amidosulphite, by a process not unduly troublesome, yields 10 per cent. of its weight, and probably much more by skill and care. In order to prepare the ammonium amidosulphite and decompose it afterwards, ammonia in excess and sulphur dioxide are led into a closed flask, fitted with a thermometer and an exit-tube dipping in mercury. To absorb the heat caused by the combination of the gases, the flask is held in a bath of brine and crushed ice, which is more effective when the flask contains some ether and is kept in motion, because then the salt does not stick to the walls of the flask as a waxy, badly-conducting coating. The rate of flow of the gases is to be regulated by the operator's ability to prevent the temperature in the flask from rising much above  $10^{\circ}$ . The inside

of the apparatus, the gases, and the ether are all to be dried before use.

When as much amidosulphite has been formed as may be wanted or be convenient to prepare, the cooling mixture in the bath is replaced by water, and a slow stream of dry hydrogen passed through the flask, whilst the temperature of the water is slowly raised to about  $70^{\circ}$  and then kept at that point for five or six hours, or so long as ammonia continues to come off in any quantity. During this operation, the ether, if used, also evaporates. The sulphamide is all formed at temperatures not higher than  $30^{\circ}$ - $35^{\circ}$ , and a higher temperature is here employed only for the purpose of destroying as much as possible of the thionic compounds which are formed along with the sulphamide and would, at a later stage, consume much silver nitrate and undesirably produce much ammonium nitrate, if present. The employment of a higher temperature than  $70^{\circ}$ , to destroy all the thionic compounds, is not possible, because then the sulphamide itself would be decomposed.

When the flask has cooled down, enough ice-cold water is poured in to dissolve all its contents other than a considerable quantity of sulphur, left by the destroyed compounds. To the yellow, unfiltered solution, which has been poured into an open vessel, barium hydroxide is added in quantity a little more than sufficient for the salts it precipitates, among which are sulphate, imidosulphite, and thiosulphate. In order to lessen the dilution of the solution of sulphamide, the barium hydroxide is used in mixed solution and crystals, as obtained by rapidly cooling a hot, concentrated solution. The precipitate is to be filtered off, though it is not very easy to get a bright filtrate, and, even when this is accomplished, the filtrate soon becomes turbid again, owing to

further production of sulphate by the decomposing salts present in it. This does not matter, however, and to the turbid filtrate silver nitrate is added, just so long as it continues to give a precipitate. The barium hydroxide will have liberated much ammonia, but a good deal of this will have evaporated during the time taken up in filtration, especially if the precipitation has been carried out in an open vessel. What remains of it interferes only temporarily with the silver precipitation and does not usually need external neutralisation. For, so much acid is formed as the result of a very rapid decomposition of the precipitated silver salts (in which they change from white to black), as to be more than enough to neutralise the ammonia remaining in the solution, and also to dissolve up any silver sulphamide that may have been thrown down at first. When the mother-liquor has become thoroughly acid or, exceptionally, has been made so by adding nitric acid, and still holds silver in solution, it is filtered from the black precipitate and just neutralised with ammonia. Any slight precipitate then formed is also filtered off and rejected; it contains no trisulphimide. The filtrate holds little else than sulphamide and ammonium amidosulphate, and if evaporated over sulphuric acid, would yield both these substances in characteristic crystals. But to isolate the sulphamide, it is to be precipitated from this solution by silver nitrate and ammonia, that is, by Traube's method. The silver sulphamide, thus obtained, is almost pure, there being no such acid matter present as is met with when the sulphamide has been prepared from sulphuryl chloride. In that case, a viscid silver salt accompanies the silver sulphamide, and, according to HANTZSCH and HOLL, can only be removed from it by a process entailing the destruction of much of the sulphamide. Even in the present case, however, the amido-

sulphate, left with the sulphamide, may cause a little difficulty, unless care be taken.

On referring to the memoir on amidosulphuric acid in the Journal of the College of Science for 1896 (9, 239-241, "amidosulphonic acid"), it will be found there stated that when an alkali is added in suitable quantity to a solution of mixed silver nitrate and potassium amidosulphate, a bright yellow, amorphous salt is precipitated, which is very probably  $\text{AgHN}\cdot\text{SO}_3\cdot\text{K}$ , and is soluble in and ultimately decomposed by excess of alkali. It is now found that, in precipitating silver sulphamide in presence of ammonium amidosulphate, as in the present case, a very small quantity of a bright-yellow substance, probably ammonium argent-amidosulphate, is apt to accompany the silver sulphamide, and that, in order to circumvent this liability and, at the same time, to avoid loss of the silver sulphamide through its solubility in ammonia in presence of ammonium nitrate, precipitation should be carried out in the following way. Having added more silver nitrate, dilute ammonia is dropped in, slowly and with stirring, until the solution is slightly alkaline. The precipitate is quickly filtered off and washed free from mother-liquor. The solution is again treated with silver nitrate and ammonia, as before, in order to see whether any more sulphamide is thrown down. This being quickly filtered off, if it be desired to obtain a sight of the yellow compound, a few drops of ammonia may be added, and dilute silver nitrate very slowly dropped in, when it will be produced.

The silver sulphamide, perhaps a little yellow after all, is to be dissolved in dilute nitric acid, ammonia added to slight alkalinity, as before, and then two or three drops of silver nitrate. After a repetition of this treatment, the precipitate is stirred up

with exactly enough dilute hydrochloric acid to decompose it, just as TRAUBE directs. The filtrate from the silver chloride, which must not be acid, gives the sulphamide in good crystals, when it is evaporated in the desiccator. It is to be recrystallised, and, since it is exceedingly soluble, the mother-liquors must be worked up, if a good yield is wanted.

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