

Ethyl ammoniumsulphite.

By

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In attempts to obtain ammonium amidosulphite, which proved successful only when made in another direction, we have found that, in absence of water and at a low temperature, ammonia and alcohol unite with sulphur dioxide and form a new salt of the composition of ammonium ethylsulphonate and yet quite distinct from it. Evidently, ammonia and alcohol react with sulphur dioxide as though they were ethylammonium hydroxide, for ammonia in the cold has no action upon ethylsulphite or upon ethyl ethylsulphonate and, when heated with the former produces ethylamine and ammonium sulphite (Carius, *Ann.*, 1859, **110**, 221), and with the latter ethylammonium ethylsulphonate (Carius, *J. pr. Ch.*, 1870 [2] **2**, 262).

Warlitz' potassium ethyl sulphite, never but doubtfully distinct from a sulphonate, has now been shown to be none other than potassium ethylsulphonate (Rosenheim and Liebknecht, *Ber.*, 1898, **31**, 405). From the experiments of Carius and from those of the chemists just named, it is also certain that ethyl sulphite does not react directly to form a salt intermediate to itself and potassium sulphite, and is thus distinguished from a sulphonate, as Carius pointed out (see also the action of ammonia, just referred to above).

But, within the last few years, a new class of alkyl metallo-sulphites has come to be known and in this class the new ethyl ammoniumsulphite must be placed. The first member to be discovered was phenyl sodiumsulphite (Schall, *Ber.*, 1892, **25**, 1875; *J. pr. Ch.*, 1893, [2] **48**, 241), formed from sodium phenoxide and sulphur dioxide; next, came methyl magnesium-sulphite, obtained by Szarvasy (*Ber.*, 1897, **30**, 1836) from magnesium methoxide and sulphur dioxide, and, lastly, methyl and ethyl sodiumsulphite and ethyl potassiumsulphite, prepared from sodium or potassium ethoxide or methoxide, as the case required, and sulphur dioxide (Rosenheim and Liebknecht, 1898, *loc. cit.*).

Schall has established that his salt is $\text{Na} \cdot \text{SO}_2 \cdot \text{OC}_6\text{H}_5$, and Rosenheim and Liebknecht have given good reasons for regarding their salts, and also Szarvasy's salt, as similarly constituted — $\text{Na} \cdot \text{SO}_2 \cdot \text{OC}_2\text{H}_5$; $\text{Mg} (\text{SO}_2 \cdot \text{OCH}_3)_2$, that is, as having a constitution complementary to that of sulphonates. Szarvasy, indeed, takes his sulphite to have a constitution analogous to that of the ethyl magnesium carbonate, which he has obtained in a similar way, but, in doing so, he ignores, what seems so well established, that sulphites behave as the analogues of formic acid and other carboxylic salts, rather than of carbonates, though producible in the same way as the latter salts.

Quite special precautions have to be taken to ensure the absence of water. Muspratt, passing "dried" sulphur dioxide and ammonia into ether, was surprised to get ammonium pyrosulphite: Carius found that "carefully dried" sulphur dioxide formed only sodium sulphite when led into sodium ethoxide dissolved in "*absolute*" alcohol (the italics are his), although,

as a fact, it does combine with the ethoxide. Both chemists had failed in their attempts to exclude water, and we, too, have failed to keep back all moisture. In 100 cc. of concentrated alcoholic ammonia, we had never much less than 80 mgm. water, but, fortunately, we could still eliminate this, as anhydrous ammonium sulphite, which is insoluble in alcohol.

The alcohol, at its final distillation from lime, was received direct into the reaction-flask, which was then closed by a dried cork provided with inlet and outlet tubes, the latter dipping into mercury as a seal. Ammonia, partially dried by passing it up a spiral tube immersed in a cooling mixture, was then sent through a series of tubes, packed with crushed and recently fused potassium hydroxide, into the alcohol in the reaction-flask, which was kept cool in a freezing-mixture. When ammonia began to freely escape through the mercury, no more of it was sent in, and a current of sulphur dioxide, well dried by sulphuric acid, passed in slowly until this gas in turn began to bubble freely through the mercury, when the current was stopped. While the sulphur dioxide was being passed into the flask, care was taken to keep the temperature of the ice-and-salt mixture, as nearly as practicable, down to -15° , and to agitate the flask. There was a double reason for keeping the temperature low, for, in the first place, a very concentrated solution of ammonia in the alcohol must be begun with, in order to get the greater part of the alcohol taken up afterwards in forming the new salt, and thus lead to the crystallisation of the latter by removal of the alcohol, in which it is quite soluble. The other purpose served by the low temperature was to prevent any of the sulphur dioxide from acting oxidisingly upon the ammonia, and thereby producing an orange-

coloured impurity (apparently nitrogen sulphide) and ammonium sulphite.

After passing the sulphur dioxide in for a short time, the turbid solution produced had to be allowed to clear and then be decanted, with as little exposure to air as possible, from a small deposit (0.5 grm. or less) of anhydrous ammonium sulphite, into another reaction-flask. This sulphite represented the small amount of moisture carried into the alcohol by the ammonia or otherwise. The introduction of sulphur dioxide being resumed, transparent four-sided prisms began to form when the ammonia was nearly saturated, and then so rapidly increased in quantity as to have dried up nearly all the solution by the time the ammonia was all gone. If at this point the operation was arrested and the flask brought to the common temperature and placed in a vacuum-desiccator, it was found to be impossible to get the crystals pure enough for analysis, because there was not only the liability of this exceedingly hygroscopic substance to condense a little moisture to contend with, but also its mother-liquor contained something in solution which remained as a viscid, non-volatilising residue which was probably pyrosulphite, $\text{Et Na S}_2\text{O}_5$. Instead, therefore, of stopping the entrance of more sulphur dioxide into the flask when all ammonia had been neutralised, the operation was continued for a much longer time until, as stated above, much sulphur dioxide passed uncondensed. By this time, the crystals had disappeared, being slowly dissolved up as the sulphur dioxide increased in quantity. Whether this was a case of mere solution in the sulphur dioxide, liquefied at so low a temperature, or was due to the formation of pyrosulphite, cannot with certainty be said.

In order to get back the salt in the solid state, the solution was poured, in portions suitable for analysis, into small flasks of ether, freshly distilled from sodium. The two liquids did not at first mix, but by gentle rotation the sulphite solution coated the flask and crystallised on its walls, while much sulphur dioxide escaped. On now pouring off the ether and washing the crystals with more ether, the salt dried rapidly in the desiccator and was then weighed in the same flask. The ether left no residue on evaporation.

The analysis of the salt was simple. Distillation with alkali gave the ammonia and alcohol, which were received in volumetric acid. After titrating for ammonia, the neutral distillate was again distilled, and the specific gravity and weight of the new distillate taken in order to determine the quantity of alcohol. The alkali sulphite in the distilling flask was heated in a pressure tube with hydrochloric acid and again rendered alkaline and distilled, in order to be certain that no amidosulphate had been formed, which was in fact the case. The sulphur dioxide was determined in a separate portion of the salt by oxidising, first, with bromine and alkali and, then, with potassium chlorate and hydrochloric acid, and precipitating sulphate by barium chloride. The quantities of salt serving for the analyses were about 2 grams each.

$\text{C}_2\text{H}_5(\text{NH}_4)\text{SO}_3$: alcohol; 36.22; ammonia, 13.38; sulph. diox., 50.39, per cent.
Found: " 35.87; " 13.35; " 49.99, "

Ethyl ammoniumsulphite is crystalline and sublimes unchanged almost completely when heated in a dry tube and without blackening. It is decomposed violently by strong sulphuric acid and also without blackening. Acids at once set

free sulphur dioxide. It is insoluble in ether, soluble in alcohol without change, and recoverable from its solution by evaporation unchanged, provided every trace of water is kept away. It is also in part precipitated from its concentrated solution in alcohol, by saturating this with ammonia at a low temperature. It is exceedingly deliquescent and is immediately decomposed by water, in which it dissolves. Its alcoholic solution at once crusts over when exposed to the air, ammonium pyrosulphite being produced. The aqueous solution or deliquesced salt smells strongly of sulphur dioxide and gives the reactions only of a sulphite in its fresh state; but from the tendency of pyrosulphite to change into trithionate, it becomes a little yellow on standing and its silver precipitate slowly changes colour. Hydrochloric acid gives no precipitate of sulphur in its fresh solution, and the acid solution loses all its sulphur as sulphur dioxide, when quickly boiled.

Szarvasy found it necessary, in preparing methyl magnesiumsulphite, to saturate the alcoholic solution with sulphur dioxide, while, for the reason above given, we found it advantageous to saturate the alcohol with sulphur dioxide in preparing the ethyl ammoniumsulphite. Rosenheim and Liebknecht, on the other hand, state that the use of any excess of sulphur dioxide in making the alkyl alkalisulphites is most carefully to be avoided, since otherwise these salts decompose into "acid" alkalisulphites. This difference between closely allied salts would be remarkable and not easy to understand if its existence could be confirmed. In absence of water, pyrosulphites, rather than acid sulphites, alone can form. But, if the unknown ethyl sodiumpyrosulphite had been the salt formed, these chemists would, presumably, not have failed to indicate the

fact. Again, if sodium pyrosulphite and ethyl pyrosulphite had been the products, then the latter would also have been noticeable as a compound new to science. Szarvasy's and our own experience and the difficulty of interpreting Rosenheim and Liebknecht's results have caused us to prepare ethyl sodiumsulphite and test its behaviour with sulphur dioxide.

Sodium, bright and clean-cut under dried ether, was quickly transferred to a little dry alcohol in a small flask until the solution thickened and became inactive on more sodium. The solution was quickly decanted, in a cold, dry atmosphere, into another flask and cooled in a freezing mixture, which caused abundant crystallisation of sodium ethoxide. Sulphur dioxide was now passed in until it was in large excess in the liquefied state. Its effect was to cause the sodium ethoxide to gradually dissolve and give place to the micaceous crystals of Rosenheim and Liebknecht's salt, until the solution had almost all dried up. After this, it appeared to have no further action. The very sulphurous mother-liquor was drained off and the flask placed in a vacuum-desiccator to dry its contents. The dry salt was weighed in the preparation-flask and then aqueous solution of potassium hydroxide poured on to it. Oxidised, first by bromine and then by potassium chlorate and hydrochloric acid, it gave 24.67 per cent. sulphur, thus, confirming the observation that the salt did not seem to be affected by excess of sulphur dioxide, for the calculated quantity of sulphur in ethyl sodiumsulphite is 24.24 p.c. We conclude, therefore, that Rosenheim and Liebknecht failed to guard sufficiently against the entrance of moisture, and that their salts are not destroyed by dry sulphur dioxide. The sulphur dioxide mother-liquor poured off in our experiment

was left standing for some time in an open flask, and was only then placed in a desiccator. It left a small quantity of sodium pyrosulphite as a white powder. The salt is therefore a little soluble in alcoholic sulphur dioxide and then by absorbing water becomes alcohol and sodium pyrosulphite.

