Products of heating Ammonium Sulphites, Thiosulphate, and Trithionate.

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What has been published upon the effects of heating ammonium sulphites and thiosulphate is but little in accordance with the results of experiments we have had to make upon these salts and upon the hardly known trithionate, in connection with an investigation of the decomposition by heat of ammonium amidosulphite. We therefore make known what we have ascertained.

Preparation of the salts used.

Ammonium sulphite, $(NH_4)_2SO_3, OH_2$.—Statements are conflicting as to whether this salt can be got from its solution by evaporation (Muspratt, *Phil. Mag.*, 1847, iii, 30, 414; Marignac, *Jahresb.*, 1857, 17; Forcrand, *Compt. rend.*, 1885, 100, 245; Hartog, *Compt. rend.*, 1887, 104, 1793; Roehrig, *J. pr. Ch.*, 1888, 37, 227). We find that a concentrated solution, charged with ammonia, can be quite successfully made to deposit the salt by cold evaporation in a potash desiccator, but to get such a solution the moderately strong solution of ammonia, which must be used, has to be kept very cold while passing in the sulphur dioxide. Dilute solutions fail to yield the salt on evaporation because too much of it suffers decomposition. Much better than evaporating is to take advantage of the lessened solubility of the salt in presence of much ammonia. Ammonia solution, sp. gr. 0.895, containing therefore about 28 grm. ammonia in 100 c.c., is to be treated in a flask with sulphur dioxide, while it is kept in motion in a mixture of ice and salt, and with the tube conveying the sulphur dioxide not dipping into the solution. The formation of a very little orange-coloured matter in the neck of the flask cannot be avoided, but this can be easily removed afterwards. When the solution has become thick with crystals, no more sulphur dioxide is to be added, although very much ammonia still remains. Even at the common temperature the crystals do not sensibly dissolve in presence of this ammonia. The salt, drained on a tile under close cover, can be dried either by filter paper or by only short exposure in the desiccator over potassium hydroxide or carbonate, salted just before with ammonium chloride. It is equivalent in quantity to about one-fourth of the ammonia taken. By long exposure in a dried atmosphere the salt becomes anhydrous without loss of ammonia. Exposed to the air, it is apparently deliquescent but in reality it evolves ammonia and thus becomes the very deliquescent pyrosulphite.

Anhydrous ammonium sulphite is readily obtained from the hydrated salt by long enough exposure in the desiccator; it is very hygroscopic.

Ammonium pyrosulphite, $(NH_4)_2S_2O_5$.—When, in the process just given for preparing the normal sulphite, the passage of sulphur dioxide is not stopped when the solution is full of crystals, these gradually dissolve up and the solution becomes greenish-yellow. Then, as it gets charged with sulphur dioxide, in the cooling mixture, the pyrosulphite crystallises out from it, in quantity equivalent to a little over one-fifth of the ammonia taken, being thrown out of solution by the sulphur dioxide. The salt can be obtained dry and pure in the same way as the normal sulphite, except that sulphuric acid, to which a little solid alkali sulphite has been added, is used in the desiccator, though it is very deliquescent and changeable when not carefully preserved from moisture. This salt is also easily obtainable by evaporating its aqueous solution, but hardly free from sulphate, and not without some decomposition, through loss of sulphur dioxide and through oxidation. It is much more soluble than the normal sulphite.

Ammonium thiosulphate.—An old solution of calcium thiosulphate, obtained by boiling lime and sulphur together in water and leaving the solution until much of the pentasulphide had been oxidised by the air, was decanted from insoluble matters, mixed with ammonium carbonate in some excess, filtered, and then freely exposed to the air for some time at 50-60°. In this way a very concentrated solution of ammonium thiosulphate was obtained, free from sulphate and other salts. The solution of this very soluble salt was then dried up to a crystalline mass in the desiccator. The well-dried crystals have been found by Lock and Kluess (*Ber.*, 1889, **22**, 3099) to be anhydrous.

Ammonium trithionate.—This salt has apparently not hitherto been prepared by any one. Being exceedingly soluble in water, it cannot be prepared by Plessy's excellent process for the potassium salt (*Ann. Ch. Phys.*, 1844, iii, 11, 182), or by its slight modification by Hertlein (*Z. phys. Ch.*, 1896, 19, 287). We therefore made the pure potassium salt by Plessy's method, precipitated the potassium from it by hydrofluosilicic acid, neutralised quickly with ammonia, and precipitated the ammonium trithionate by absolute alcohol and dried it in the desiccator. This very deliquescent and changeable salt cannot be kept long in good condition, but it was used by us when freshly prepared and while still almost free from sulphate.

Effects of heating the salts.

The process.—The salts were heated in an oil-bath, in a subliming vessel consisting of a test-tube, 15 cm. long and about 15 mm. in internal diameter. The tube was closed by a caoutchouc stopper, and a very slow current of dried nitrogen through the tube was maintained during the heating and cooling. The salt, usually about 4 grm., was contained in an open slender bottle, about 6 cm. long, having a platinum wire attached to it for lowering it into and lifting it out of the subliming tube. The tube was immersed in the oil to the level of the mouth of the bottle inside, so as to cause all dry sublimates to collect in the tube above this level. When, as in the case of the hydrated normal sulphite, the heating was divided into stages, the bottle was transferred between these to a second subliming-tube. The heating of the oil was conducted very slowly, so that the temperatures mentioned which were those of the oil, may be accepted as being very nearly those of the salts at the time.

In describing the effects of heating them, the salts are taken in the inverse order of that followed above, in accordance with usage. This is done because of the nature of the products.

Ammonium trithionate.—This salt is hardly affected until the temperature is above 150°, and at 160-170° it steadily decomposes into sulphur dioxide and a residue of ammonium sulphate and unfused sulphur. The non-fusion of the sulphur is remarkable and only to be referred to the presence of minute quantitities of impurities. It all dissolved readily in carbon bisulphide, and crystallised out on evaporating the solvent.

It can hardly be doubted but that *ammonium tetrathionate* (and *pentathionate,* if it can exist) would decompose in the same way as trithionate. *Ammonium hyposulphate* (*dithionate*) has been shown by Heeren (*Pogg.*, 1826, **7**, 55), and more definitely by Kluess (*Ann.*, 1888, **246**, 194) to first become anhydrous, if not already so when heated, and then to decompose at about 130° into sulphur dioxide and a residue of ammonium sulphate.

Ammonium thiosulphate.—Zeise, in 1824 (*Gm. Hbk*) found this salt to be converted by heat into water, ammonia, and a sublimate of sulphur, much thiosulphate again and sulphite, and a little sulphate. This result must have been obtained by rough heating. A much more weighty statement is that made by Spring (*Ber.*, 1874, **7**, 1159), namely, that the dry salt can be sublimed unchanged, intermediate dissociation being admitted. We have found it to decompose very slowly at 150°, the main products being a sublimate of anhydrous normal sulphite and a residue of sulphur unfused, as in the case of the trithionate. But, also very small quantities of hydrogen sulphide and ammonia passed off in the current of nitrogen, and the sublimate contained a very little of a salt having some of the properties of trithionate and which did not strike the violet colour with ferric chloride given by a thiosulphate. Analysis of the sublimate and of that part of the salt which remained mixed with the sulphur when the progress of the decomposition was arrested after only half of it had been decomposed, gave results that showed the former to be essentially anhydrous normal sulphite, and the latter unchanged thiosulphate:—

	Ammonia	Sulphur	
$(NH_4)_2SO_3$	29.31	27.59	per cent.
Sublimate	27.54	27.55	„
$(NH_4)_2S_2O_3$	22.27	43.24	„
Residue	20.69	42.31	„

The main decomposition of the thiosulphate is in full agreement with the relation of thiosulphates to sulphites. Very interesting is the production of a little ammonia and hydrogen sulphide, in connection with the relation of trithionate to thiosulphate as its thio-anhydride (Spring):—$2(NH_4)_2S_2O_3 = 2NH_3 + SH_2 + (NH_4)_2S_3O_6$. When ammonium thiosulphate is rapidly and more strongly heated, ammonia is lost and sulphur sublimes; then as a matter of course and of no significance, thiosulphate and even trithionate are produced on adding water to the mixed sublimates.

Ammonium pyrosulphite.—We did not get this exceedingly deliquescent salt into the tube ready for heating before it had condensed some moisture, and to this we attribute part of the results obtained. Change went on slowly in the salt at 130° and somewhat faster at 150°. At first there was little else than a slight but steady evolution of sulphur dioxide, and this continued though very feebly, to the end and while a sublimate forming. The sublimate was pyrosulphite in one experiment; in another, it was this salt mixed with a very little anhydrous sulphite. But there was a considerable residue, more than one-third of the weight of the salt taken, consisting of sulphate, trithionate, sulphur, and apparently some tetrathionate. There was no sulphite or thiosulphate. The tetrathionate, the sulphur, and the sulphur dioxide were very probably derived from decomposition of trithionate by moisture. From a consideration of the results it seems almost necessary to assume that perfectly dry pyrosulphite sublimes unchanged (with no doubt intermediate dissociation), and that the presence of a little moisture causes it to decompose partly into sulphate and trithionate.

Anhydrous ammonium sulphite volatilises at about 150°, yielding a sublimate of the same salt, or rather, a pseudosublimate, for the salt surely dissociates when heated.

Hydrated ammonium sulphite.—According to Muspratt, this salt all volatilises when heated, no sulphate being produced, and yields water, then much ammonia, and finally a sublimate which, judging, from its properties, is ammonium pyrosulphite. We observed the following effects of gradually heating it in a very slow current of dried nitrogen. At about 90°, the salt moistened and escape of ammonia became quite evident, and at a little above 100° distillation of water also took place; both water and ammonia continued to escape in noticeable quantities for $2^1/_2$ hours longer, when the temperature for some time had been 120°; up to this, a very little sublimate only had formed and matters were now almost at a standstill. The quantity of the salt heated was about 4 grm., and this had now lost one-fifth of its weight, the residue having the composition expressed by $(NH_3)_{10}(SO_2)_6(OH_2)_7$, equivalent to a mixture or combination of the three salts, hydrated sulphite (39.4%), anhydrous sulphite (34.1%), and pyrosulphite (26.5%), dividing equally among themselves the sulphur dioxide. Some repetitions of the experiment gave almost the same results. Calculation and the results of one experiment gave the following numbers :—

	Ammonia	Sulphur dioxide	
$(NH_3)_{10}(SO_2)_6(OH_2)_7$	25.00	56.47	per cent.
Found	24.65	56.20	„

If, in the formation of this complex, no longer losing material quantities of ammonia and water, only these products had been given off, the residue should have been 84½ per cent. of the hydrated normal sulphite, whereas it proved to be little more than 79 per cent., in consequence of volatitisation of some of the (dissociated) salt, made manifest by the production of a little sublimate.

After renewing the heating in a fresh subliming-tube, allowing the temperature to rise slowly from 120° to 150°, the residue had almost all disappeared in two hours, while an abundant dry sublimate had deposited. For some time during this heating, sulphur dioxide steadily escaped, but practically ceased to do so long before sublimation was finished. The residue left when sulphur dioxide was no longer coming off, proved on analysis to be normal sulphite again, but only half hydrated, $2(NH_4)_2SO_3, OH_2$. The sublimate, also, now and at the finish, consisted of normal sulphite, apparently anhydrous though found to be a little hydrated because it is very hygroscopic and had unavoidably some exposure to the air while it was being scarped out of the tube into the weighing bottle.

Hydrated ammonium sulphite, therefore, becomes by gradual heating to 120° converted one-third into the anhydrous salt, and one-third into pyrosulphite, by loss of water and ammonia ; and then the nearly stable complex of these salts with the other third of the original salt becomes converted into the nearly anhydrous normal sulphite, between 120° and 150°, sulphur dioxide and water escaping. The presence of water is essential to the occurrence of both changes; dry ammonium pyrosulphite partly sublimes as such at 150° and partly changes into sulphate and trithionate, as already described. Heating in the open tube, and more rapidly, Muspratt's results will be got, for then weter is more quickly expelled, and some pyrosulphite can deposit as a sublimate.