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## Nitrilosulphates.

By

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*History.*—Nitrilosulphates were discovered in 1845, by Fremy, who named them sulphammonates. Their sulphonic constitution was made evident by Claus and Koch in 1869, and their nitrilic constitution by Berglund in 1875, when they received the name of nitrilosulphonates. Finally, Raschig rendered the constitution of these salts still more certain in 1887. These chemists, it should be mentioned, added nothing to the experimental facts concerning the nitrilosulphates which Fremy had made known, but Claus and Koch determined the nature of the 'sulphazidates,' salts derived from Fremy's 'neutral sulphazotates' by hydrolysis; Raschig proved the constitution of the last-named salts, which by sulphonation become the sulphammonates; and Berglund established the constitution of the 'sulphamidates' into which the sulphammonates are transformed by hydrolysis; all the experimental interconnections of these salts, here relied on, having been ascertained

by Fremy himself. The recognition of the constitution of the nitrilosulphates by Fremy was a moral impossibility, for their discovery had come, so to say, much before its time.

*Name.*—The reason for the substitution of the name nitrilosulphates for that of nitrilosulphonates, chosen for these substances by Berglund, has been stated on a former occasion (this Journal, 1896, 9, 220). As nitriles they are sulphates—nitrilosulphates therefore. Suitable alternative names are aminetrisulphonates and trisulphamates.

*Preparation.*—Ammonium nitrilosulphate,  $4\text{NH}_3, 3\text{SO}_3$ , cannot be obtained by the union of ammonia with sulphur trioxide; for that results in the production of the imidosulphates, which are not resolvable by heat into nitrilosulphate and ammonia, since the less ammoniated  $\frac{2}{3}$ -normal salt, instead of breaking up in this way—boils freely at about  $355^\circ$ , under reduced pressure, with very little decomposition and no production of nitrilosulphate (this Journal, 1894, 6, 55). Nitrilosulphates are only to be prepared by sulphonation of hydroximidosulphates. Fremy made known two ways in which this can be accomplished, of which however only one admits of general application. This is to treat the hydroximidosulphate with sulphur dioxide in presence of a base, a process which resolves itself in practice into treating the corresponding nitrite in this way, since the hydroximidosulphate has itself to be prepared by a similar sulphonation of the nitrite. The other way of preparing nitrilosulphates by sulphonation is to add a nitrite to an excess of solution of a pyrosulphite, when in the case of the potassium salt, the nearly insoluble nitrilosulphate soon separates. Other nitrilosulphates, being more soluble, can hardly be obtained directly in this way, but, as Fremy has shown, a solution of the ammonium salt thus prepared, very impure though it will be, can

be made to yield potassium nitrilosulphate by double decomposition.

*Ammonium salt.*

Nothing has been done concerning this interesting salt,  $N(SO_3NH_4)_3, 2OH_2$ , since Fremy described it, but as its existence has been ignored since the time of the publication of its discovery until now, we hold it important to again introduce some account of it, derived from Fremy's memoir (*Ann. Chim. Phys.*, 1845, 15, 408) into chemical literature. In presence of a large excess of ammonia a concentrated solution of ammonium nitrite is submitted to the action of a current of sulphur dioxide until abundant precipitation of crystals has occurred in the solution kept sufficiently cool. The washed and dried salt gave Fremy the following numbers on analysis, indicating the presence of one molecule of water of crystallisation :

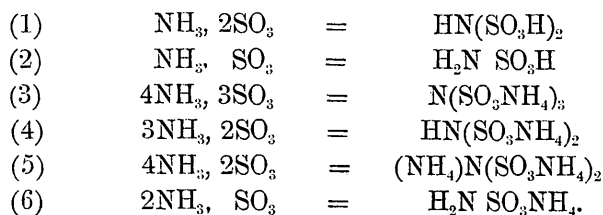
	Sulphur.	Nitrogen.	Hydrogen.
$N_4H_{14}S_3O_{10}$ ;	29.45	17.18	4.29
Found ;	30.2	15.7	4.5

Since the potassium nitrilosulphate contains two mols. water, it is probable that the ammonium salt contains the same, and that when Fremy determined the sulphur the salt had, like the sodium salt, lost some of its water during its stay in the desiccator. We write, therefore, the formula of the salt,  $N(SO_3NH_4)_3, 2OH_2$ .

Ammonium nitrilosulphate is in minute crystals which have only a slight taste, and which are somewhat sparingly soluble in water, but so much more so than the potassium salt that Fremy suggested that its solution might be used as a qualitative reagent for potassium salts. It is not volatilised by heat but decomposed into sulphate. It is a very unstable salt, being liable in the solid state to decompose (hydrolyse) suddenly with a hissing sound,

charring paper in contact with it. We have already published (this Journal, 1900, 13, 307) our success in sulphonating ammonium nitrite into hydroximidosulphate by a method, which carried farther, gave Fremy the nitrilosulphates.

Ammonium nitrilosulphate has the interest attached to it of being one more compound of ammonia with sulphur trioxide to be added to those recognised. There are six such compounds:—



Of these the second is amidosulphuric acid and the sixth its ammonium salt (this Journal, 1896, 9, 219); the first imidosulphuric acid, known only in unstable solution (this Journal, 1894, 6, 51); the fourth is its  $\frac{2}{3}$ -normal ammonium salt (parasulphatammon of Rose); and the fifth, polymeric with the sixth, is its normal ammonium salt (sulphatammon of Rose; this Journal, 1894, 6, 53); and the third is ammonium nitrilosulphate here described. These six compounds can all be derived the one from the other, backwards as well as forwards, except the nitrilosulphate which cannot be re-formed from the others although itself the most convenient source of them. Nitrilosulphuric acid would be the seventh of these compounds, heading the column as  $\text{NH}_3, 3\text{SO}_3$ , if it could exist in the free state.

#### *Potassium salt.*

The potassium salt,  $\text{N}(\text{SO}_3\text{K})_3, 2\text{OH}_2$ , is familiar to those who have occupied themselves with the study of Fremy's sulphazotised salts, being one of the most insoluble of potassium salts, even

more so than the perchlorate (Fremy). It forms slender needles of pearly lustre which in crystallising fill its mother-liquor. The work of later investigators has added nothing to the account of it given by Fremy, except that the crystals are rhombic (Raschig and Fock).\* His analyses gave results which agree well with calculation for the true composition of the salt, though not with his own formula for it. By preference he prepared it by passing sulphur dioxide into a solution, not too concentrated, of the nitrite and the hydroxide. With the neglect of details characteristic of his celebrated memoir, he fails however to mention the essential potassium hydroxide. Probably on account of this, later workers, have only made use of his other process, which consists in mixing solutions of the nitrite and pyrosulphite.

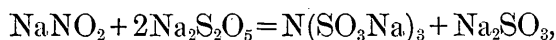
*Sodium salt*,  $N(\text{SO}_3\text{Na})_3, 5\text{OH}_2$ .

A strong solution of sodium pyrosulphite poured upon solid sodium nitrite furnished Raschig (*Annalen*, 1887, 241, 180 and 229) with a useful solution of the nitrilosulphate, although it contained much hydroximidodisulphate, sulphite, and unchanged nitrite; sodium hydroxide he represented also to be present, but that could not have been the case (this Journal, 1900, 13, 284). Sodium nitrilosulphate being very soluble in water, he did not isolate it in the solid state. We have found that instead of three mols. pyrosulphite, which was the quantity used by Raschig to two mols. nitrite, at least four mols. must be taken if most of the hydroximidodisulphate is to be sulphonated.† By preparing

\* Misled by the faulty translation in the *Annalen* (1845, 56, 342) of Fremy's paper, Claus and Koch supposed that he had said that red fumes were evolved when the salt is heated. Fremy's statement is that the salt does not evolve red fumes, which is correct.

† Claus and Koch found it best to take still more pyrosulphite when working with the potassium salts (*Annalen*, 1869, 152, 336), and they were right, for in the case of that insoluble nitrilosulphate, great excess of sulphite did not matter; here it does.

from the carbonate (using this in hydrated crystals, along with only half its weight of water, and saturating with sulphur dioxide) a fresh and pure solution of pyrosulphite as concentrated as possible, pouring this solution upon the nitrite dissolved in its weight of water, one mol. nitrite to every two mols. carbonate taken, and shaking the flask in cold water for a short time to moderate the rise of temperature, a solution is obtained which will in an hour or two deposit a small quantity of sparkling crystals of the nitrilosulphate, and give more when it is evaporated over sulphuric acid. The equation,

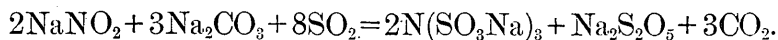


represents the change but this would take many days to become complete, long before which time the nitrilosulphate would have all decomposed. In the mixed solution only a few hours old, some hydroximosulphate, as well as nitrite, is still present.

The only satisfactory method of preparing sodium nitrilosulphate is a slightly modified form of that employed by us to get the imidosulphate (this Journal, 1894, 6, 65). In that process, which is after all only a development of Fremy's method of preparing the ammonium salt, the nitrilosulphate is prepared and at once allowed to hydrolyse into imidosulphate, whereas in the present case its hydrolysis is to be prevented. There a moderately concentrated solution met the end in view, whilst here the greatest possible concentration is wanted, because evaporation of the solution afterwards, though sometimes successful, is a very uncertain operation, in consequence of the short existence which can be assured to the nitrilosulphate. A solution therefore is prepared of two mols. nitrite to three mols. carbonate, so concentrated that the water is scarcely more than twice the weight of the anhydrous carbonate (for example, 10 grams nitrite, 8.5 grams hot water, and

62.2 grams carbonate crystals). Sulphur dioxide is passed rapidly into the solution in a flask continuously shaken. When, after a time, the solution grows hot the flask is immersed in cold water, and when it thickens, through temporary separation of acid carbonate, vigorous shaking of the flask is to be maintained without intermission. As the quantity of the acid carbonate suspended in the warm solution ( $50^{\circ}$ - $60^{\circ}$ ) lessens, the rate of current of the sulphur dioxide should be reduced and the action of the solution upon litmus paper closely watched. At the moment the solution reddens the litmus, the entrance of more sulphur dioxide must be stopped, for should acidity to lacmoid paper also be reached through the addition of much more sulphur dioxide, the nitrilosulphate will at once hydrolyse into imidosulphate. During the final slow sulphonation, the solution will generally grow cold enough to begin to deposit small crystals of the nitrilosulphate, recognisable by their brilliant lustre; these will increase largely in quantity at the temperature of the air. Without waiting too long, it is safer to add two or three drops of concentrated solution of sodium hydroxide, sufficient to render the solution faintly alkaline to litmus. It is possible to get more of the salt by evaporating the mother-liquor over sulphuric acid.

That the reaction proceeds sharply in accordance with the following equation is known from the quantity of imidosulphate which such a solution can be made to furnish:—



In consequence, however, of the great solubility of the nitrilosulphate the crystals obtained amount to barely more than one-fifth of the total quantity; still, even that is 120 per cent. of the weight of nitrite taken. The crystals hold 21.8 per cent. of water, or  $5\text{OH}_2$ . Of this quantity it has twice been possible to

remove 15.5 per cent. by exposing the salt in a vacuum over sulphuric acid, after which the salt has hydrolysed and thereby fixed the rest of the water. The production of the unused pyrosulphite, shown in the above equation, is necessary for the safe and prompt sulphonation of all hydroximidosulphate.

Sodium nitrilosulphate crystallises in short thick prisms which melt when heated and decompose in their water of crystallisation into sulphates. The crystals cannot be long preserved under any circumstances, soon suffering decomposition and becoming opaque and acid, even in their own mother-liquor after it has been made alkaline. That is, the sodium salt is more unstable than the potassium salt. It is neutral to litmus and must be soluble in about its own weight of water, to judge from the amount of it left in the mother-liquor in its preparation, although here, no doubt, the pyrosulphite also in solution will affect its degree of solubility.

For analysis, it was drained on the tile after washing with a little strong ammonia-water, in which it is less soluble than in water. Partial water determinations have already been referred to.

	Sulphur.	Sodium.	Nitrogen.
$N(SO_3Na)_3, 5OH_2$ ;	23.24	16.71	3.39
Found;	23.05	16.54	—
”	22.96	—	3.64
”	23.25	16.68	—
”	23.17	—	3.45
”	—	16.55	—

*Double salts.*

*Potassium sodium nitrilosulphate*,  $N(SO_3)_3 K_2Na$ .—Raschig obtained this salt by adding a solution of potassium chloride



gradually to a crude solution of sodium nitrilosulphate (p. 5). We have obtained the same salt, which is like the sodium salt in appearance and like the potassium salt in being nearly insoluble. According to Raschig it is anhydrous and occurs either as a sparkling sand or in hard crystals, the size of pinheads and of adamantine lustre.

*Barium salts.*—By dissolving the sodium salt in a strong solution of barium chloride faintly alkaline with ammonia, a flocculent precipitate is obtained which becomes dense and crystalline on standing. It is sparingly soluble in water and very unstable. It probably contains sodium but we have not analysed it. Fremy obtained barium ammonium and barium potassium salts which he could only imperfectly analyse because of their instability. They resembled the barium sodium salt, and from the results of his analyses appear to have been two-thirds barium and one-third ammonium or potassium salt, with water of crystallisation.

*Lead salts.*—According to Fremy, very unstable lead salts containing potassium or ammonium are obtainable.

