XLIII.—*Potassium Nitrito-hydroximidosulphates and the Non-existence of Dihydroxylamine Derivatives.*

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Like potassium nitrate (Trans., 1894, **65**, 523), potassium nitrite forms double salts with the potassium hydroximidosulphates (sulphonates); and the non-recognition of their existence has given rise to mistaken notions as to the nature of the products produced by the sulphonation of nitrous acid.

Potassium Nitrite and 2/3 Normal Hydroximidosulphate, $KNO_2,HON(SO_3K)_2$.—The sparing solubility of 2/3 normal potassium hydroximidosulphate in water is so little affected by the presence of potassium nitrite, that it crystallises out again almost pure on cooling a hot solution, even if this contains as much as one-sixth of its weight of the nitrite; when however, more nitrite than this is present, a salt separates which is a compound of the hydroximidosulphate with a mol. of the nitrite, and the same double salt is formed in the cold when the hydroximidosulphate is triturated with a strong solution of the nitrite in excess. If precautions are taken against the hydrolysis of the very unstable hydroximidosulphate, this salt can be dissolved at 70° in as little as 3·8 times its weight of a 22 per cent. solution of nitrite, and on cooling, the solution deposits the crystalline double salt in quantity equivalent to about 12/13 of the hydroximidosulphate.

Whilst the hydroximidosulphate itself crystallises in hard, rhombic prisms with $2H_2O$, its compound with the nitrite forms silky, asbestos-like fibres, which are anhydrous; the compound salt differs also from potassium nitrite in not being deliquescent, but in other properties, is indistinguishable from a mixture of its component salts. It can be recrystallised from a hot 10 per cent. solution of potassium nitrite. It is neutral to litmus and very soluble in water, but its solution soon deposits crystals of the 2/3 normal potassium hydroximidosulphate, unless it is very dilute. In any case, the hydroximidosulphate can be separated from the nitrite by precipitating it with barium hydroxide. Like a hydroximidosulphate (Trans., *loc. cit.*), the solid salt, when digested with a highly concentrated solution of potassium hydroxide, is converted into sulphite and nitrite. When acidified, its solution becomes yellowish, and soon effervesces from escape of nitrous oxide, leaving potassium hydrogen sulphate in solution; this effect is due to the hydroximidosulphate being a sulphonated hydroxylamine, and hydroxylamine, with nitrous acid, decomposing into nitrous oxide and water. It decomposes explosively when heated—more so than does the hydroximidosulphate by itself—giving off almost colourless gases and white fumes.

The compound salt can be purified from other salts or from alkali by recrystallisation from a sufficiently concentrated potassium nitrite solution, but from its own mother-liquor it must be separated by draining on a tile, such draining being very effective because of the felted, fibrous form of the salt, its non-deliquescent nature, and the hygroscopic character of a solution of potassium nitrite. The analysis of the salt was made in the usual way described in our previous papers on hydroximidosulphates and other sulphonated nitrite derivatives. By boiling its solution with an acid, most of its sulphur appears as ordinary sulphate, but not quite all; so that, in estimating the sulphur, the solution must be hydrolysed for some hours at 150° under pressure.

	Potassium.	Sulphur.
Found	33·14	17·95 per cent.
$K_8HN_2S_2O_9$ requires	33·10	18·06 ,,

There are other ways in which the potassium nitrito-2/3 normal hydroximidosulphate may be formed, all consisting essentially in producing the hydroximidosulphate by sulphonating a small portion of the potassium nitrite in a concentrated solution. Thus, the following mode of working will give good results with certainty, but it may be widely deviated from with due consideration and precaution, provided only that a concentrated solution of nitrite be employed. Potassium nitrite, 30 grams; potassium hydroxide, 10 grams; water, 50 to 100 grams, are to receive a current of sulphur dioxide freely until crystals begin to form, the containing flask being all the time agitated in a cooling bath of ice and brine. The sulphur dioxide is now passed in more slowly for some time longer, and then stopped. After half an hour, the salt deposited from the solution is collected and drained on a tile. Its mother liquor is alkaline to litmus, but not to rosolic acid (presence of sulphite, absence of alkali); the well-drained salt itself is only faintly, if at all, alkaline to litmus. The double salt is also produced when to an ice-cold, nearly saturated solution of potassium nitrite, a similar solution of potassium pyrosulphite is very slowly added until crystallisation begins, and the solution is allowed to stand for some time. Prepared in this way, the compound salt is liable to be contaminated with a little nitrilosulphate and sulphite. The experiment just described was made first by Raschig, but he attached to it a significance unlike that here presented. Discussion of his views will be found towards the end of this paper.

There is yet another way in which this potassium nitrito-hydroximidosulphate can be produced, which it is of interest to mention, because it illustrates the decomposibility of potassium 5/6 normal hydroximidosulphate into the normal and 2/3 normal salts. While the 2/3 normal salt dissolved in 16 per cent. or stronger solutions of the nitrite, crystallises out only in combination with nitrite, the 5/6 normal salt, when dissolved in a nitrite solution of even 50 per cent., for the most part crystallises out again uncombined; generally, however, with this strength of nitrite solution, a little fluffy or cotton-like, lustreless matter also separates. If now, to this fluffy matter, suspended in its cold mother liquor carefully decanted from every particle of the crystals of the 5/6 normal salt, a hot solution of this 5/6 normal salt in 50 or even 40 per cent. nitrite be poured in, a relatively large quantity of the fluffy matter is obtained, and not the hard prisms of the 5/6 normal salt. Under the microscope, the fluffy matter proves to be crystalline, and when drained on a tile it has a silvery lustre; on analysis, it is found to be the nitrito-2/3 normal hydroximidosulphate, only slightly impure from the presence of a little 5/6 normal hydroximidosulphate and nitrite. Thus, in place of potassium 33·10, and sulphur 18·06, per cent., we found in it 33·79 and 18·35 respectively, together with an alkalinity equal to 1·09 per cent. potassium. If dissolved in hot 12 per cent. nitrite solution, it recrystallises as the pure double salt. It is thus apparent that in a very concentrated solution of nitrite containing the 5/6 normal salt dissolved in it, there is unstable equilibrium between the tendency to yield $HON(SO_3K)_2,KON(SO_3K)_2,H_2O$ again, and that to form $HON(SO_3K)_2,KONO$.

Sodium nitrite forms a compound with sodium 2/3 normal hydroximidosulphate, which has not been further examined, principally because of its great solubility in sodium nitrite solution.

Potassium Nitrite and Normal Hydroximidosulphate, $KNO_2,2KON(SO_3K)_2,4H_2O$.—This compound salt is only obtainable from a strongly alkaline solution, for when the normal hydroximidosulphate is dissolved in a hot concentrated solution of the nitrite, only the 5/6 normal hydroximidosulphate crystallises out on cooling, just as it would do in the absence of nitrite. In order to crystallise out either the normal hydroximidosulphate (Trans., *loc. cit.*) or its combination with nitrite, free alkali must be present in some quantity. When, however, too much alkali is present, a little of it deposits with the normal salt or with the nitrito-normal salt (in place apparently of water of crystallisation, Trans., *loc. cit.*), and then lessens the capacity of the normal salt to combine with nitrite. The double salt is readily obtained by dissolving normal hydroximidosulphate nearly to saturation in a hot (70°) solution consisting of 33—66 parts nitrite and 3—5 parts hydroxide to 100 parts water, and cooling. Usually, it forms lustrous, silky fibres, like those of the 2/3 normal double salt, but radiating from points to form voluminous, soft, spherical masses. When the solution is more strongly alkaline, the double salt separates as nearly opaque, spherical granules, sometimes with long fibres growing out from them. Under the microscope, these granules are seen to have also a radiating fibrous structure, and to represent the soft, voluminous spheres highly condensed; probably the latter always begin their growth from a minute granular nucleus. The double salt can only be purified for analysis by pressing it on the porous tile, when the soft spheres become a felted, lustrous cake, and the hard, white granules crumble down like masses of wax.

	Potassium.	Sulphur.	Alk. potassium.
Silky, found	35·21	16·23	9·92 per cent.
$K_7N_3S_4O_{16},4\cdot4H_2O$	35·14	16·43	10·04 ,,
Granular, found	33·99	15·90	9·20 ,,
$K_7N_3S_4O_{16},6H_2O$	33·89	15·85	9·68 ,,

The varying amount of water is only the recurrence of what we have recorded in the case of normal potassium hydroximidosulphate. The double salt is exceedingly alkaline; its alkalinity we estimated by means of decinormal acid and litmus.

Like the previously described double salt, it is but little soluble in concentrated nitrite solution, although freely soluble in water, which decomposes it into its constituent salts, and also decomposes one of these, the normal hydroximidosulphate, into alkali and crystals of the 5/6 normal salt. When heated, it decomposes suddenly, but gently, without fusing or scattering, and evolves slight red fumes but no white ones. By this behaviour, it was easily distinguishable from the 2/3 normal double salt, and also from any other hydroximidosulphate which, simple or combined with nitrite, contained less than its K_7 to S_4. By dissolving the nitrito-2/3 normal hydroximidosulphate in a hot concentrated solution of nitrite containing sufficient alkali, the nitrito-normal hydroximidosulphate can be readily obtained on cooling the solution.

Potassium Nitrite and 5/6 Normal Hydroximidosulphate.—We have obtained three compounds of the 5/6 normal salt with nitrite, one being $7KNO_2,2K_5H(NS_2O_7)_2,3H_2O$. By using an almost saturated solution of potassium nitrite containing a little potassium hydroxide, and dissolving in it, by heat, the 5/6 normal hydroximidosulphate, a compound is obtained in minute, fibrous crystals, very lustrous when dry; this is decomposed by water, but may be recrystallised from a saturated nitrite solution. The same salt can be obtained also by dissolving the nitrito-normal hydroximidosulphate in a hot, almost saturated solution of nitrite.

When heated, it is feebly explosive. Its composition approaches that indicated by the formula given above. For analysis, it was only air-dried on a tile; in the desiccator, it would probably have lost its 3 per cent. of water (= $3H_2O$), and then approached in composition Fremy's *sulphazite*:

	Potassium.	Sulphur.	Alk. potassium.
Original salt, found.....	36·81	14·35	4·80 per cent.
Recrystallised	36·68	14·47	4·51 ,,
$K_{17}H_2N_{11}S_8O_{42},3H_2O$...	36·87	14·20	4·34 ,,

A second double salt, $3KNO_2,K_5H(NS_2O_7)_2,H_2O$, was prepared by dissolving 1 mol. of 5/6 normal salt and 1·4 mols. of potassium hydroxide in a hot 65 per cent. nitrite solution, and cooling. In appearance, it resembled the other compound salt.

	Potassium.	Sulphur.	Alk. potassium.
Found..................	36·17	15·07	4·51 per cent.
Calculated	36·81	15·06	4·60 ,,

A third double salt, anhydrous, $7KNO_2,3K_5H(NS_2O_7)_2$, was not prepared synthetically, but was obtained by treating an almost saturated solution of the nitrite with alkali and sulphur dioxide, and adding alkali again after the sulphonation, imitating a process of Fremy's. On filtering the heated solution from much crystalline 5/6 normal hydroximidosulphate mixed with a little of its combination with nitrite, and allowing the mother liquor to cool, it became almost filled with tiny prisms of a compound answering to the above formula:

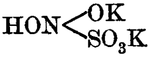
	Potassium.	Sulphur.	Alk. potassium.
Found	36·94	16·37	4·96 per cent.
Calculated	36·99	16·51	5·05 „

This salt was quickly resolved by water into nitrite and crystals of the very sparingly soluble 5/6 normal hydroximidosulphate.

The varying proportions in which potassium nitrite and the 5/6 normal hydroximidosulphate unite would possess but little interest, were it not for the fact that they have evidently been severally met with and taken to be salts of specific constitution by Fremy and by Raschig.

Non-existence of Dihydroxylaminesulphonates.

Fremy believed in the existence of less sulphonated derivatives of potassium nitrite than his *sulphazite* (see next paper), itself less sulphonated than his *sulphazotates* (hydroximidosulphates), and attributed his failure to find them to the fact of their excessive solubility. Claus held much the same views, and believed that by adding to an aqueous solution of potassium nitrite an alcoholic solution of sulphur dioxide in not too large a quantity, he had obtained an impure crystallisation of a salt, $ON{\cdot}SO_3K$ (*Ber.*, 1870, 4, 508). He did not prove this to be the case, but what he did publish about his product is sufficient to show that it was the compound of potassium nitrite with 2/3 normal hydroximidosulphate we have described in this paper. A repetition of his experiment gave us this double salt, together with much ethyl nitrite. Raschig regarded Claus's preparation as essentially the same as one of his own salts, to which he gave the constitution of basic dihydroxylaminesulphonate derivatives with the following formulæ:



$$\mathrm{HON}{<}\begin{matrix}\mathrm{OK}\\ \mathrm{SO_3K}\end{matrix}$$

and

$$\begin{matrix}\mathrm{HO}\\ \mathrm{SO_3K}\end{matrix}{>}\mathrm{NON}{<}\begin{matrix}\mathrm{SO_3K}\\ \mathrm{OK}\end{matrix}.$$

These he prepared by partial sulphonation of the nitrite in known ways. They both yielded crystals of a hydroximidosulphate when dissolved in a little water, and differed in no essential particular from nitrito-hydroximidosulphates. We found that hot solutions of nitrite and a hydroximidosulphate, on cooling, deposited an apparently homogeneous crop of crystals of almost the same composition and properties as one or other of Raschig's salts. Raschig gave two ways for preparing the salt having the second of the formulæ just given, and in these ways we have obtained the nitrito-2/3 normal hydroximidosulphate already described in this paper, but mixed with a little potassium sulphite. This impurity accounts for the alkaline reaction of Raschig's preparation and the presence in it of a little more than K_3 to S_2.

He obtained the other salt (K_2 to S) only once, and in the form of white crusts, when working unsuccessfully for hydroximidosulphate in Claus's way, the other main product being imidosulphate, that is, hydrolysed nitrilosulphate, as he himself pointed out. Following Fremy's method, we have obtained—also by sulphonating nitrite—a product qualitatively like Raschig's salt, although differing a little from it quantitatively, and, at the same time, like the second salt compounded of nitrite and 5/6 normal hydroximidosulphate described by us on page 436. The percentages found by Raschig were potassium, 36·84, and sulphur 15·50.

When Raschig's salt was dissolved in water and acidified, it gave nitrous oxide as the only gaseous product, whilst ours gave also some nitric oxide. This fact might have served to render incorrect the application of our formula to his salt, but for the evidence there is that it was mixed with a little sulphite, which would have reduced any nitric oxide. Its mother liquor, on further evaporation, gave, we are told, so much sulphite along with the next crop of the salt itself, as to cause its rejection. The presence of sulphite in less quantity in the first crop of crystals will have been masked by the oxidising action of the nitric oxide in becoming nitrous oxide. That sulphite was present in Raschig's preparation well accords also with the fact that potassium hydroxide added in excess precipitated potassium sulphite, for, although hydroximidosulphate is itself decomposed by the most concentrated solutions of potassium hydroxide into sulphite and nitrite, this decomposition is slow, and the sulphite is deposited only after some time. Raschig's preparation, when dried on a tile, was only a powder—that is, presumably, was not obviously crystalline—a point which also indicates an impure salt. Since the potassium and sulphur are in the same ratio in the two salts, quantitative analysis would hardly have made its presence known.* Inspection of Raschig's formulæ is of itself sufficient to prevent their being accepted as in accordance with the facts; for, from these formulæ, both salts should be strongly alkaline, whilst, in reality, one is neutral. Above all, it is hardly credible that dissolution in cold water should suffice to cause monosulphonated nitrogen to become disulphonated.

Raschig held his two salts to be identical with Fremy's *potassium sulphazite* and *sulphazate* respectively; but the nature of Fremy's salts

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* Of the $3KNO_2$ of our formula, only 1 mol. can give nitric oxide and that only to the extent of two-thirds of its nitrogen, the other third becoming nitric acid. Raschig's analysis indicates the presence of only 3/4 mol. active nitrite. The quantity of hydrated sulphite required to be present is therefore only 5·2 per cent. of the mixed salts.

will be found, we believe, more precisely given in the paper following this. The point we would here insist on is that Raschig's preparations, judged by their chemical behaviour, have no claim to be considered as *dihydroxylamine* derivatives, being in every way indistinguishable from synthetically prepared compounds of nitrite and hydroximidosulphates. Dihydroxylamine salts have as yet only a hypothetical existence, and are likely to remain so, for the double linking of the oxygen atom with the tervalent or quinquevalent nitrogen atom seems always experimentally to make or break itself in a single act, notwithstanding its bipartite character.

Raschig, in his researches on Fremy's sulphazotised salts, obtained, besides those we have just discussed, two other salts of undetermined constitution, both of which were most probably also nitrito-hydroximidosulphates. They may therefore be noticed here, although Raschig did not represent them to be dihydroxylamine derivatives. Yet they evidently closely resembled the other two in properties. One was isomeric with potassium hyponitrososulphate (Pelouze's salt), and also with his (K_2 to S) dihydroxylamine salt, allowing for difference in hydration, and the other was isomeric with potassium 5/6 normal hydroximidosulphate. Each could be obtained but once, and they only call for any detailed notice because of the theoretical importance given to them as isomerides of other salts. The first referred to above was mistaken by Raschig for Pelouze's salt (hyponitrososulphate), but that salt it certainly was not (Trans., 1895, **67**, 453). It was prepared by dissolving nitric oxide in solution of potassium sulphite and hydroxide, and evaporating to a small volume until crusts formed. If we assume that air or nitric peroxide was not excluded, the conditions were present for getting a nitrito-hydroximidosulphate, for, as we hope to show in a paper which will shortly follow this, nitrous fumes passed into potassium sulphite solution generate hydroximidosulphate freely, together with nitrite.

The other salt, isomeric with 5/6 normal hydroximidosulphate, was obtained in Raschig's attempt to form the 2/3 normal salt by passing sulphur dioxide into a solution of potassium nitrite and hydroxide and leaving the mixture for a day. These, too, are conditions for the formation of nitrito-hydroximidosulphate. Now both products were decomposed by water in such a way as to yield hydroximidosulphate, whilst in other ways they behaved as compounds of nitrite with one of these salts. The behaviour of the product isomeric with hyponitrososulphate was indeed exceptional, in that, when dissolved in water containing a little alkali, it gave the 2/3 normal hydroximidosulphate, although, according to our calculation, it should have given the 5/6 normal salt; moreover, it also gave, in hot alkaline solution, a little nitrous oxide, which only hydroxyamidosulphate is known to give. These peculiarities we may attribute to partial hydrolysis having occurred in the very unstable salt before these experiments were made.

The calculated formula for the isomeride of hyponitrososulphate as a nitrite compound is $3KNO_2,K_5H(NS_2O_7)_2,2H_2O$, and such a compound we have described on page 436; that for the isomeride of the 5/6 normal hydroximidosulphate treated as being a nitrite compound is $3KNO_2,6K_2HNS_2O_7,5K_5H(NS_2O_7)_2$, which in water should give crystals of $K_2HNS_2O_7,2H_2O$. This compound salt we have failed to obtain, but its occurrence can be readily accepted as possible. Its assumed existence affords a much more satisfactory explanation of the nature of this salt of Raschig's than that we were able to offer in our paper on hydroximidosulphates already referred to.

	Potassium.	Sulphur.	
Nitroso-isomeride, found......	35·72	14·40	per cent.
Calculated........................	36·05	14·75	,,
D. and H.'s salt, found	36·17	15·05	,,
Oximido-isomeride	33·04	21·23	,,
Calculated........................	32·91	21·54	,,

For the present, the existence of isomerides of Pelouze's salt and Fremy's *basic sulphazotate* must be regarded as no longer even probable.