

On the Reduction of Nitrites to Hydroxyamine by Hydrogen Sulphide.

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The solution of an *alkali nitrite*, saturated with hydrogen sulphide, and then acidified with hydrochloric or sulphuric acid, yields sulphur, nitric oxide, and ammonia, but no hydroxyamine, the presence of this being incompatible with the presence of what is known as *free* nitrous acid. When the escaping gases are collected out of contact with air, they slowly deposit sulphur, and do so more quickly still, when bubbled through water into the air, in consequence of reactions between hydrogen sulphide, nitric oxide, and oxygen,—but still no hydroxyamine appears.

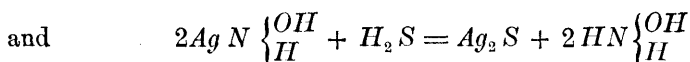
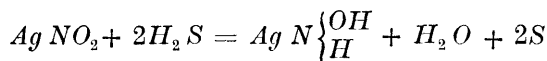
But when *silver nitrite* in water is treated with hydrogen sulphide, then besides the sulphur, nitric oxide, and ammonia, still abundantly formed, (and also silver sulphide), there is found a considerable quantity of hydroxyamine. On filtering off the silver sulphide, adding hydrochloric acid to convert the hydrosulphides into hydrochlorides, and evaporating to dryness, there is obtained a mixture of ammonium and hydroxyammonium chlorides. (Heating the filtrate before adding an acid causes destruction of the hydroxyamine by the hydrogen sulphide).

Two estimations were made of the quantity of hydroxyamine in the solution, after this had been heated with hydrochloric acid. Silver nitrite, 0.6926 gram, was found, by titration with iodine, to have yielded about one-sixth of its nitrogen as hydroxyamine; while, in another case, 0.0644 gram yielded as much as three-elevenths of its nitrogen in this form.

Mercurous nitrite, supposed not to exist, but which will be described in a future communication, has been prepared by the authors, and found also to yield hydroxyamine when treated with hydrogen sulphide. But this salt forms dense, hard crystals, and is exceedingly insoluble in water, and thus becomes difficult to decompose fully, even by soluble chlorides, including hydrochloric acid. It, accordingly, resists for a long time complete decomposition by hydrogen sulphide, so that when that which appears to be only the mercury sulphide and sulphur precipitate is boiled with water, a nitrous smell is observed, due, no doubt, to decomposition of some residual nitrite.

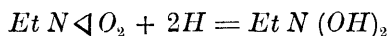
The green solution prepared by mixing alkali nitrite with copper sulphate also yields hydroxyamine when treated with hydrogen sulphide.

It will hence be seen that those nitrites of which the metals,—mercury, silver, copper,—have especially marked affinities for nitrogen, and which nitrites, therefore, have a certain stability in presence of acids, are capable of being reduced to hydroxyamine. In large part, indeed, even these nitrites are decomposed by the hydrogen sulphide, so as to yield only the products of the decomposition of this acid by water and additional hydrogen sulphide; but the rest appears to act as follows:—

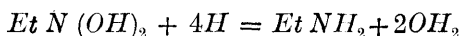


As a means of the preparation of hydroxyamine, the action of hydrogen sulphide upon a nitrite has no apparent value. The interest of this reaction lies in the light it may help to cast upon the constitution of the oxygen compounds of nitrogen. Experiments made in our laboratory, and already published in the *Journal of the Chemical Society of London*, serve to show that the metals of the zinc-tin class convert *nitric acid* into *ammonia*, and not hydroxyamine, when another acid is absent; and into *hydroxyamine*, without ammonia, when acting in conjunction with hydrochloric or sulphuric acid (J.C. S., 47, 615); and, further, that in the conversion of nitric acid to hydroxyamine, no *nitrous acid*, *nitric peroxide*, or *nitric oxide* shows itself as an intermediate product. It therefore, remained uncertain whether an (inorganic) *nitrite* could be converted into hydroxyamine. By the reaction of the nitrites of the silver class of metals with hydrogen sulphide this uncertainty is now removed.

In connection with the subject of this paper, the well-known behaviour of the nitro-hydrocarbons is of interest to consider. The application of reducing agents, if appropriate, converts them to *amines*, but never to *hydroxyamines*. Yet the paraffin members of the series yield simple or substituted hydroxyamines by certain treatment. Plainly, it must be impossible by simple reduction to convert the *nitro*-compound into the corresponding *oximido*-compound, because of the difference in valency between the nitroxy- and oximido-radicals and therefore the reaction proceeds probably as follows:—

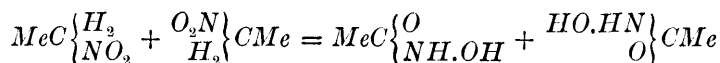


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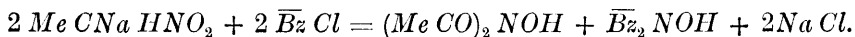


But when, under special conditions, the hydrocarbon radical is made to suffer change, it becomes possible to form an oximido compound (Kissler), or, at least, hydroxyamine itself (V. Meyer). In these cases, the hydrocarbon acts as the reducing agent upon the nitroxyl. Thus,

nitroethane, at 140°, and in presence of water and hydrochloric acid, yields hydroxyamine, passing probably through the following change:—



in which acet-hydroxamic acid results from the interaction of two molecules of the nitroethane, and then, as usual under such circumstances, suffers hydrolysis into hydroxyamine and acetic acid. Again, by the interaction of sodium-nitroethane and benzoic or acetic chloride, diacet-hydroxamic acid is actually secured as the end-product:—



In this case, each oximido-radical finds ready for it two univalent radicals, in place of the one united to the nitroxyl, in consequence of the separation of the sodium and chlorine as salt.

It is thus evident, that, under suitable conditions, both metal nitrites (or nitrous acid itself) and organic nitrites (nitronites) reduce to hydroxyamines. It is, further, seen that the conversion of inorganic nitrites to hydroxyamine lends no support to the view that they have an *oxylic* constitution; because organic nitrites, beyond doubt non-oxylic, also reduce to oximido-compounds.

