V.—*Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide.*

By EDWARD DIVERS and TAMEMASA HAGA.

THE solution of an alkali nitrate, saturated with hydrogen sulphide, and then acidified with hydrochloric or sulphuric acid, yields sulphur, nitric oxide, and ammonia, but no hydroxylamine,* the presence of this being incompatible with that 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 on bubbling through water into the air, in consequence of reactions between hydrogen sulphide, nitric oxide, and oxygen, but still no hydroxylamine appears.

When, however, *silver nitrite* suspended in water is treated with hydrogen sulphide, besides the sulphur, nitric oxide, and ammonia, still abundantly formed, and the silver sulphide, a considerable quantity of hydroxylamine is also produced. On filtering off the silver sulphide, adding hydrochloric acid to convert the hydrosulphides into hydrochlorides, and evaporating to dryness, a mixture of

---

* NOTE BY EDWARD DIVERS *on the dropping the "l" out of the word hydroxylamine.*—It seemed to me unnecessary to urge anything in justification of my action when I ventured to use the spelling, hydroxyamine, in a paper which appeared in the Society's Journal, Trans., 1885, 597; but the Editor's note attached to that paper having shown me my mistake, I now make good the omission. If, as is certainly the case, the composite names in use in chemistry should convey their significance equally to the ear as to the eye, then it seems much better to call oxyammonia *hydrox'yamine* or *hydrox'amine* than to call it *hydroxyl'amine*, and thus avoid accenting an insignificant syllable. It is true that *meth'ylamine*, *phen'ylamine*, and the like, are also commonly pronounced *methyl'amine*, *phenyl'amine*, but there is no difficulty in giving these words their correct and useful sounds, whereas although the pronunciation *hydrox'ylamine* is not an impossible one, the "l" in it proves unpleasantly *de trop*. As we say *hydroxyacetic acid* for *oxyacetic acid*, and similarly throughout the series of hydroxyl compounds, so should we say *hydroxyamine* for *oxyammonia*. Already we do say *hydroxyammonium*, and *hydroxamic acids*. Then, again, we say *nitrosamines*, and not *nitrosylamines*. There is another advantage in dropping the "l," for by doing so the chance is avoided of confounding the last syllable of *oxyl* with the first one of *xylene*, as in *nitroxylene*. (*Cf.* A. H. Allen, *Chem. News*, **54**, 83.)

[The term "hydroxylamine" is one which occurs in every text-book and manual, is universally employed by chemists, and is applied to a compound very generally used by those engaged in organic research. There appears to be no reason why we should discard this name, and adopt a *new word* to designate this well-known substance. I may point out that the argument adduced by Dr. Divers, in this note, in favour of dropping the "l" from "hydroxylamine" applies with equal force to methylamine, ethylamine, benzylamine, &c., which would become *methyamine*, *ethyamine*, and *benzyamine* respectively.—THE EDITOR.]

ammonium and hydroxyammonium chlorides is obtained. Heating the filtrate without first adding an acid causes destruction of the hydroxylamine by the hydrogen sulphide.

Two estimations were made of the quantity of hydroxylamine 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 hydroxylamine, whilst in another case, 0·0644 gram yielded as much as three-elevenths of its nitrogen in this form.

In the Society's *Abstracts of Proceedings*, p. 95, there is a preliminary note by us on the reaction between mercurous nitrate and nitric oxide and between mercurous nitrate and alkali nitrites, in which the formation of hydroxylamine is described, together with separation of metallic mercury, and some yellow prismatic crystals of undetermined nature. Soon afterwards one of us succeeded in getting the supposed non-existent *mercurous nitrite*, and this we then identified with our yellow prisms found in the reactions just referred to. Unavoidable delay in completing the examination of mercury nitrites has caused us to put off publishing this paper until now; it is expected that that on mercury nitrites will soon be ready.

Mercurous nitrite yields just the same products as silver nitrite when it is treated with hydrogen sulphide; but as this salt occurs in hard crystals, and is exceedingly insoluble in water, it is difficult to decompose it completely by soluble chlorides including even hydrochloric acid. Accordingly, it resists decomposition by hydrogen sulphide for a long time, and when what appears to be mercury sulphide (and sulphur) is boiled with water, a nitrous odour is observed and mercury goes into solution, due no doubt to the decomposition of some residual nitrite.

It was to the above reaction between mercurous nitrite and hydrogen sulphide that the formation of hydroxylamine was due, when we treated mercurous nitrate first with nitric oxide or alkali nitrite, and then with hydrogen sulphide—mercury nitrite being formed in the reaction we were investigating, and hydroxylamine only by the hydrogen sulphide reducing this nitrite. We cannot indeed affirm positively that hydroxylamine is absent from the mercurial solution before hydrogen sulphide is added, because it is not easy to find a reagent capable of precipitating the mercury—*mercuric* as well as *mercurous*—without decomposing any hydroxylamine that might be present. As we know, however, that nitrite is present in abundance dissolved in the acid mercury solution,* and as

---

* Evidence of this will be submitted in our forthcoming paper on *mercury nitrites*, together with an account of the formation of the nitrite, and the precipitation of the metallic mercury.

this would certainly give hydroxylamine with hydrogen sulphide, whilst the production of this base from mercurous nitrate and nitric oxide alone is most improbable, there is now no ground whatever for believing that it is thus formed.

On leaving metallic copper in contact with silver nitrite in water, a bluish-green solution is obtained, from which a little hydroxylamine can be formed by treating it with hydrogen sulphide. A much larger yield can be got from the green mixture of solutions of copper sulphate and potassium nitrite.

From the account we have given of the behaviour of hydrogen sulphide towards nitrites, it may be seen that those nitrites of which the metals—mercury, silver, copper—have especially well marked affinities for nitrogen, and which therefore have a certain stability in presence of acids, are capable of being reduced to hydroxylamine. In great part, indeed, even these nitrites are decomposed by the hydrogen sulphide in such a way as to yield merely the products of the decomposition of this acid by water and additional hydrogen sulphide; but the rest appears to react as follows:—

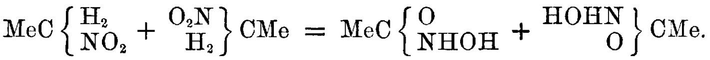
$$AgNO_2 + 2H_2S = AgNH{\cdot}OH + H_2O + 2S;$$
$$2AgNH{\cdot}OH + H_2S = 2NH_2{\cdot}OH + Ag_2S.$$

As a means of preparing hydroxylamine, the action of hydrogen sulphide on a nitrite has no apparent value. The interest of it lies in the light it may help to throw on the constitution of the oxygen compounds of nitrogen. Experiments made in our laboratory, and already published in the Society's Journal, serve to show that the metals of the zinc-tin class convert nitric acid into ammonia, and not hydroxylamine, when no other acid is present; and into hydroxylamine without ammonia, when acting in conjunction with hydrochloric or sulphuric acid (Trans., 1885, 615), and further, that in the conversion of nitric acid to hydroxylamine, no nitrous acid, nitric peroxide, or nitric oxide, shows itself as an intermediate product (Trans., 1883, 461, 462). An alkali nitrite brought suddenly in contact with hydrochloric acid and zinc sometimes yields a little hydroxylamine (Trans., 1883, 454), but, as pointed out, the probable conversion of the nitrous acid into nitric acid and nitric oxide before it comes in contact with the zinc, leaves the point doubtful whether the little hydroxylamine obtained does not come from nitric instead of from nitrous acid. Thus, it has been left uncertain whether an inorganic nitrite could be converted into hydroxylamine. By the reaction of the nitrites of the silver class of metals with hydrogen sulphide, this uncertainty is at length removed.

In connection with the subject of this paper, it is of interest to consider the well-known behaviour of the nitrohydrocarbons. The application of reducing agents, if appropriate, converts them to amines, but never to hydroxylamines. And yet the paraffin members of the series yield simple or substituted hydroxylamines by appropriate 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-radicles; the reaction therefore proceeds probably as follows:—

$$\mathrm{EtN{\lhd}O_2 + 2H = EtN(OH)_2,}$$
$$\mathrm{EtN(OH)_2 + 4H = EtNH_2 + 2OH_2.}$$

But when, under special conditions, the hydrocarbon radicle is made to undergo change, it becomes possible to form an oximido-compound (Kissler), or at least hydroxylamine itself (V. Meyer). In these cases, the hydrocarbon acts as the reducing agent on the nitroxyl. Thus, nitroethane at 140°, and in presence of water and hydrochloric acid, yields hydroxylamine, passing probably through the following stage:—



$$\mathrm{MeC}\left\{\begin{matrix}\mathrm{H_2}\\ \mathrm{NO_2}\end{matrix}\right. + \left.\begin{matrix}\mathrm{O_2N}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{CMe} = \mathrm{MeC}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{NHOH}\end{matrix}\right. + \left.\begin{matrix}\mathrm{HOHN}\\ \mathrm{O}\end{matrix}\right\}\mathrm{CMe.}$$

in which acethydroxamic acid results from the interaction of 2 mols. of the nitroethane, and then, as usual under the circumstances, suffers hydrolysis into hydroxylamine and acetic acid. Again, by the interaction of sodium nitroethane and benzoic or acetic chloride, diacethydroxamic acid is actually obtained as the end-product:—

$$\mathrm{2MeCNaHNO_2 + 2BzCl = (MeCO)_2NOH + Bz_2NOH + 2NaCl.}$$

In this case, each oximido-radicle finds ready for it two univalent radicles in place of the one united to the nitroxyl, in consequence of the elimination of the sodium and chlorine as sodium chloride.

It is thus seen that, under suitable conditions, both nitrites of the metals and organic nitrites (nitronites) reduce to hydroxylamines. It is further seen that the conversion of inorganic nitrites to hydroxylamine lends no support to the view that they have an oxylic constitution, because organic nitrites, beyond doubt non-oxylic, also reduce to oximido-compounds.