

LXV.—*On the Behaviour of Stannous Chloride towards Nitric Oxide, and towards Nitric Acid.*

By EDWARD DIVERS and TAMEMASA HAGA.

THE following account of an investigation we are carrying on, into the constitution of nitric acid and some of the products of its reduction, may serve to illustrate further the statement concerning some of the processes of reduction enunciated in a paper just presented to the Society by Mr. Shimidzu and one of us. That statement is, that a mixture of nitric acid with hydrochloric or sulphuric acid exerts a specific action upon certain metals, an action which is not a mere combination of the separate actions of the two acids. It may also, we hope, when it has been continued in a second communication on the subject, which we are preparing to lay before the Society, serve to throw light on the constitution of oxy-nitrogen compounds.

Reaction between Nitric Oxide and Stannous Chloride.

Every chemist is supposed to know that when nitric oxide is passed into a hydrochloric acid solution engaged in dissolving tin,

ammonia and hydroxyamine are produced. Strictly speaking, however this is by no means the case. We assert that, in the change that goes on, *not a trace of ammonia is formed*. Experience to the contrary must have been all vitiated by neglecting to exclude air while the gas was in contact with the mixture, and to use pure nitric oxide. Hydroxyamine is formed, but if the nitric oxide never comes in contact with oxygen, not a trace, as we have said, of ammonia is formed. V. Dumreicher has already shown (Abstr., 1882, 361) that acid stannous chloride will of itself convert nitric oxide to hydroxyamine; whether he then found ammonia or not we cannot learn. This will have depended upon the care with which he excluded air. But his observation was of great interest at the time, as serving to show what little foundation there was for the hypothesis of the action of nascent hydrogen in explaining the formation of hydroxyamine from nitric oxide by treating it with tin and hydrochloric acid. So far, indeed, as we can ascertain by experiments which we have made, the presence of the metal does not directly help to form hydroxyamine, and is of no service but to generate stannous chloride. It is objectionable on two grounds: it leaves the solution charged with unused stannous chloride whenever the preparation of hydroxyamine is stopped; and, secondly, the hydrogen it produces carries off the nitric oxide that would otherwise lie on the surface of the solution and be absorbed.

Tin and hot concentrated hydrochloric acid do not sensibly destroy hydroxyammonium chloride. This is our experience, and it confirms that of Mr. Shimidzu and one of us, as to the want of action of zinc and sulphuric acid upon hydroxyamine. Further, *stannous chloride in acid solution has no action upon hydroxyammonium chloride*, even when boiled with it; that is, for a reasonable time; an aqueous solution could itself not be boiled very long without suffering some change. Were either tin and hydrochloric acid, or stannous chloride, capable of converting hydroxyamine into ammonia, what we assert concerning the non-production of ammonia from nitric oxide by tin and hydrochloric acid could not, of course, be true. According to v. Dumreicher, however, "at a temperature of 100°, hydroxyamine is quickly and completely reduced to ammonia by excess of stannous chloride" (*loc. cit.*).

Coming now to the use of stannous chloride, our experience is, that with exclusion of air, *not a trace of ammonia is formed by its action upon an acid solution of hydroxyamine*. In working, we prefer to use a mixture of ferrous sulphate, nitric acid, and sulphuric acid as the source of the nitric oxide. It yields the gas in a pure state, and the generator can be charged and worked so as to furnish easily, except for a short time at first, a gentle stream of the gas for 24 hours

at a stretch. To destroy any nitric peroxide, formed through entrance of traces of air into the generator, the gas is sent through a wash-bottle of potassium hydroxide solution. This bottle is scarcely necessary, however, as reaction between ferrous sulphate and the acids does not begin in the cold; and before starting the disengagement of nitric oxide, a current of hydrogen is sent through the whole series of flasks and bottles until all air has been driven out. Only then is the evolution of nitric oxide commenced and passed into the apparatus, the current of hydrogen being at the same time discontinued. The remote end of the arrangement is provided with a wash-bottle as a guard against any reflux of air. When the process is finished, or when it has to be interrupted, the current of nitric oxide is stopped, and its place taken by one of hydrogen again, until all nitric oxide has been chased away. The flasks of tin chloride may then be opened with impunity, air having no effect upon the hydroxyamine already formed, not even when stannous chloride is still present, and being so, goes on changing into the stannic salt by contact with the air.

The reaction between acid stannous chloride and nitric oxide is not quite simple, however. The greater part of the nitric oxide becomes hydroxyammonium chloride, but a part of it is always converted into nitrogen. No nitrous oxide is formed. Since much of the nitric oxide passes unabsorbed, we could not well take the proportions of it to the hydroxyamine formed at the same time. But we many times collected it in quantity, the nitric oxide we were using being tested and found pure, as from its source it was sure to be.

Stannous chloride can be readily and completely, but slowly, changed to stannic chloride by the gas. Some interesting colour-changes are always observable, which serve to indicate the completion of the passage to stannic chloride. They are due, no doubt, to the presence of a trace of iron. Soon after the gas begins to pass, the solution becomes slightly greenish-brown, and so continues until all stannous chloride is used up by the gas: the colour then changes to a faint yellow. If, before all stannous chloride is destroyed, the current of nitric oxide is replaced by one of hydrogen, the solution is bleached; but if all the tin is stannic chloride, the solution does not lose its slight yellow colour by treatment with hydrogen. The yellow colour we suppose to be due to ferric chloride, the brown to the nitric oxide compound with ferrous chloride, the bleaching to the dissociation of this compound by the physical action of the hydrogen. We sometimes succeed in getting hydroxyammonium chloride in quantity equivalent to nine-tenths of the stannous chloride converted to stannic chloride, but generally we get less, at times much less. The reason of this we do not know. We have tried the effect of ferric chloride upon the reaction, and find it to be without noticeable action.

The nitrogen observed seems to us quite sufficient in quantity to account for the stannous salt converted to stannic, over and above that quantity needed for the hydroxyamine.

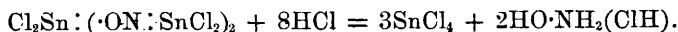
There is a remarkable fact about the reaction between nitric oxide and stannous chloride, we have yet to mention. *At a temperature of fully 100°, there is no action between nitric oxide and acid stannous chloride solution.* The stannous chloride remains unchanged for hours together, and neither nitrogen nor hydroxyamine is formed. The only thing we have noticed is always a trace of ammonia in experiments at 100°, and this, we are inclined to believe, is due to some other cause than this reaction alone. At 90°, the action is still exceedingly small, but as the temperature descends from about 80°, it becomes rapidly greater with the descent.

We have tried cooling the tin-solution by a freezing mixture, but have not succeeded in getting better results than at the ordinary temperature. Further experiments are needed, to be sure that a low temperature does not favour the reaction.

In order that nitric oxide should become hydroxyammonium chloride, it is essential that it should enter into combination with either the stannous chloride or the hydrochloric acid. Of these two, it is much more likely to unite with the former. The following representation seems probable:—



and—



Reaction of Nitric Acid with Hydrochloric Acid and Stannous Chloride.

When nitric acid is in presence of enough water to prevent any reaction taking place between it and hydrochloric acid, it is not perceptibly acted upon by stannous chloride. It may be left for a day or two mixed with these reagents, and remain, as well as the stannous chloride, unchanged. We have not yet established this fact by quantitative estimation, air having been allowed access to the mixture in our experiments hitherto, but we have no reason to believe that it is incorrect.

If such a mixture is sufficiently dilute, it may even be boiled without change, but if not too dilute, reaction is thus set up. Another way of bringing about reaction in such a dilute solution, is to add sulphuric acid, already slightly diluted so that the heating effect of mixing it with water may be avoided, since that alone would afford an explanation of its action. It is thus seen that the addition of

sulphuric acid, by diminishing the weakness of the solution in acid, serves to induce the reaction between the tin salt and the nitric and hydrochloric acids.

When dilute nitric acid added to the solution of stannous chloride in hydrochloric acid is not too dilute, reaction between them proceeds and continues until either the stannous chloride has all become stannic chloride, or until the solution has become too dilute in hydrochloric acid. In the latter case, we believe that we can cause the reaction to go on again, by passing hydrochloric acid gas into the solution, but we have not tried that yet. We have only at present added sulphuric acid as mentioned above with very favourable results. We have not succeeded, however, in destroying all nitric acid.

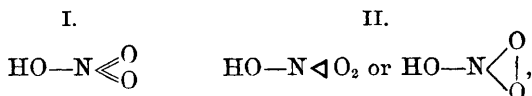
The reaction which takes place results in the conversion of so much of the nitric acid as is decomposed into hydroxyammonium chloride and nothing else—no ammonia and no gaseous body, provided the stannous chloride remains in excess. This statement is in direct opposition to that made by v. Dumreicher,* which is, that “acid stannous chloride acting on nitric acid yields hydroxylamine, but the reaction proceeds further, and the *hydroxylamine is nearly simultaneously reduced to ammonia*.” When the stannous chloride is in insufficient quantity, the conversion of the last portion of it is followed, first, by the solution becoming yellow and smelling of nitrosyl chloride, and then by an effervescence of nitrous oxide. If, on the disappearance of this yellow colour, more stannous chloride is at once added, the solution is at once bleached; and if this additional quantity of stannous chloride is insufficient, the liquid again becomes yellow after a time. The phenomena observed in this case, in fact, strongly remind one of those noticed by Vernon Harcourt, in a solution of hydrogen peroxide and hydrogen iodide to which sodium thiosulphate is added each time coloration by iodine reappears (this Journal, **20**, 460). When we proceeded in this way, the solution soon became charged with nitrous oxide, which escaped with effervescence on stirring.

From what we have said, it will, we think, be seen that nitric acid, as such, is not attacked by stannous chloride, the formation of hydroxyamine taking place from a product of the reaction between nitric and hydrochloric acids. Now, the reaction known to occur between these acids yields chlorine and nitrosyl chloride, and the question here needs to be answered, if we are to trace the nature of the production of hydroxyamine, whether these are primary or secondary products of the reaction. Could we answer this question by ascertained facts, we should, we expect, be in a position to throw

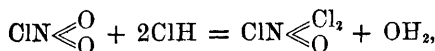
* Abstract of his paper in this Journal.

light on the constitution of nitric acid, as to whether its nitrogen is tervalent or quinquivalent.

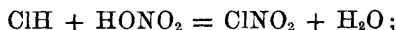
Our work, however, has not yet been carried to such a point. If nitric acid has the constitution I, we see no simple way of



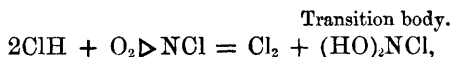
explaining the formation of nitrosyl chloride, for, admitting it to be produced by the splitting up of a transition-body, ONCl_3 , how are we to account for the formation of this body? Why, as in the equation—



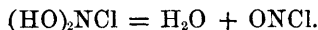
should the hydrochloric acid give its chlorine to nitrogen in exchange for oxygen, when the nitrogen cannot even, *ex hypothesi*, retain this chlorine? But if, as one of us has already suggested in a paper on the constitution of some non-saturated oxygenous salts, formula II is the correct one, a perfectly satisfactory account of the reaction can be given. First, of course, on either view, there is, as a part of the change,—



then follows (nitrogen being tervalent), in consequence of the powerful oxidising property of nitroxyl chloride,



and lastly,—



We, therefore, until further investigations have been made, hold the opinion, that the reaction between nitric acid and hydrochloric acid does not produce some as yet unknown substance, having its nitrogen quinquivalent, which is then converted by stannous chloride to hydroxyammonium chloride, but that nitrosyl chloride and chlorine are produced, as established by Tilden. There will, then, be the chlorine uniting with one part of the stannous chloride, and the nitrosyl chloride uniting—both nitrosyl and chlorine, with more stannous chloride. Finally, the nitrosyl compound with stannous chloride will react with hydrochloric acid, as already described of nitric oxide.

If we can succeed in converting all the nitric acid into hydroxyammonium chloride, this method will probably be found very

satisfactory for preparing this salt readily, and free from ammonium chloride. There is a chance of succeeding by passing hydrochloric acid gas into the solution, a method which, as we have said, remains yet for us to try.

In our next communication, we hope to be able to report on this point—as also on the reaction of stannous chloride with nitrites, nitric peroxide, nitrosyl sulphate, ethyl nitrate, and other compounds.

Stannous sulphate lying in dilute sulphuric acid has not yet given us either ammonia or hydroxyamine with nitric oxide, air and hydrochloric acid being both excluded. The stannous sulphate is slowly oxidised, and we suppose that it converts the nitric oxide to nitrogen, but this we have not yet tested. Neither have we succeeded in getting hydroxyamine by the action of stannous sulphate upon nitric acid. Longi has lately published a volumetric method of estimating nitric acid by means of stannous sulphate and a little hydrochloric acid. We have not ourselves proceeded to a full examination of the reaction.

When a mixture of nitric and hydrochloric acids acts upon metallic tin, ammonia is formed as well as hydroxyamine. But ammonia is always formed when nitric acid alone acts upon tin, and in accordance with what is stated in the paper "On the Specific Action of mixed Sulphuric and Nitric Acids upon Zinc," we consider that two actions proceed at once—one being the direct action of the nitric acid on the tin, giving rise to ammonia and oxides of nitrogen; the other being the specific action of nitro-hydrochloric acid on the tin, giving rise, not to ammonia, but to hydroxyamine. The formation of ammonia, as well as hydroxyamine, when ethyl nitrate is used, as in Lossen's original method, is, no doubt, due also to the action of the metal upon the ethyl nitrate or nitric acid derived from it. We are confident that stannous chloride will produce no ammonia from ethyl nitrate, although we have not yet tried it. Von Dumreicher has got a yield of 90 per cent. hydroxyamine from ethyl nitrate by means of stannous chloride, but he makes no mention of ammonia not having been produced (judging, that is, from the abstract of his paper in this Journal).

We may here call attention to the facts, that whilst metallic iron always forms ammonia from nitric acid, whether another acid is present or not, ferrous salts produce nitric oxide and no ammonia, so distinct is the action of a metal from that of its reducing salts.

In a paper "On the Production of Hydroxylamine from Nitric Acid," one of us has described an experiment in which even more than 80 per cent. of nitric acid was converted to hydroxyamine by means of tin and a concentrated solution of hydrochloric acid. With the

help of Mr. Shimidzu, that experiment has been repeated, and has again given 80 per cent. of the nitric acid as hydroxyamine.

In the paper referred to in the preceding paragraph, the production of hydroxyamine by means of aluminium was described, and the peculiarity pointed out that hydroxyamine is only found when the hydrochloric and nitric acids have been for some time in action upon the metal. It was there also suggested that the presence of aluminium chloride might therefore be an important factor in this production of hydroxyamine. Since that paper was published, one of us, with the assistance of Mr. T. Shimidzu, has tried the effect of having much aluminium chloride with the mixed acids when they are poured upon the metal, and found this salt to exert no apparent influence upon the production of hydroxyamine. The peculiarity referred to—that of the lateness of the production of this substance, must, therefore, be due to some other circumstance, such as the change in activity towards the acids which the aluminium certainly experiences in the course of its dissolution.
