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LXVI.—*On the Constitution and Reactions of Liquid Nitric Peroxide.*

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E.

THERE are only two constitutional formulæ for liquid nitric peroxide that have sufficient likelihood of being true to need consideration. The one represents it as formed by the union of the nitrogens of two molecules of the peroxide as it exists at high temperatures, $O_2N{\cdot}NO_2$. The other represents it as nitrosyl nitrate (Odling), $ON{\cdot}O{\cdot}NO_2$ or $(NO)NO_3$.

In favour of the first formula may be advanced its symmetrical character, and the probability that in combining, the two NO_2-groups will unite symmetrically. Against it is the fact, that when two nitrogen-atoms have once united, they do not readily separate again, as is seen in nitrogen itself, nitrous oxide, diazo-compounds, and the hydrazines.

In favour of the latter formula, there is the reaction of the peroxide with water and alkalis, by which nitrite and nitrate are formed. We question, however, whether this reaction takes place in the simple manner supposed, and intend, indeed, to test the matter experimentally. It is quite likely that the reaction is—

$$2OH_2 + 3N_2O_4 = 4NO_3H + 2NO,$$

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the nitric oxide then forming, in presence of a base, a nitrite at the surface of the liquid with the assistance of the oxygen in the air. If, however, it can be shown, that in absence of all free oxygen nitric peroxide forms, with alkalis, nitrate and nitrite in molecular proportions, this will still be insufficient to prove that it is nitrosyl nitrate. Its action upon alkali may well be similar to that of chlorine, half of it taking metal, the other taking metaloxyl :—

$$PbO + N_2O_4 = NO_2{\cdot}Pb{\cdot}O{\cdot}NO_2$$

Exner has suggested that the reaction he observed as taking place between silver nitrite and nitroxyl chloride,

$$AgNO_2 + ClNO_2 = AgCl + N_2O_4$$

(this Journal, **25**, 1072), was in favour of the constitution of the peroxide being nitrosyl nitrate. But this reaction only favours this view so long as nitrites are treated as oxylic salts, AgONO. When they are regarded as haloïd salts, $Ag{\cdot}NO_2$, it no longer does so.* The silver and chlorine unite together and leave one NO_2 to unite with the other as usual.

The reaction of the peroxide with sulphuric acid, as described by Lunge, is the only evidence that has yet been given of the peroxide being nitrosyl nitrate. In that reaction it forms nitrosyl sulphate and nitric acid—

$$(NO)NO_3 + H_2SO_4 = (NO)HSO_4 + HNO_3.$$

We think that facts recently ascertained by us, will be admitted to go far in assisting to determine the constitution of liquid nitric peroxide.

Action of Nitric Peroxide upon Mercury.—Rectified nitric peroxide was used, contained in sealed tubes, which were broken at the point when the contents were wanted. It was added to the mercury in a tube filled with dried carbon dioxide. The tube containing the two

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* *Note by Edward Divers.*—I may be permitted to point out that in the discussion of my paper "On the Constitution of some Non-saturated Oxygenous Salts" (no doubt in consequence of its having been necessarily only read in abstract), it was a mistake to represent me as basing any part of my argument, as to the constitution of nitrites, upon such slight decomposition as takes place between silver nitrite (also silver sulphite) and phosphorus oxychloride. That action I recorded as an experimental fact, at the same time expressing my belief that it had only occurred in consequence of the presence of a trace of moisture. The action will then, of course, have been $6AgNO_2 + OPCl_3 = 3AgCl + OP(OAg)_3 + 3N_2O_3$. It could hardly have been anything else, and it has no value as evidence on the point in question. My argument was simply this: nitrites do not produce nitrosyl chloride with oxychloride of phosphorus; if they did, the fact would be a convincing proof of their oxylic constitution, whilst that they do not must cast doubt upon the truth of this view of their constitution.

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liquids was sealed and left for an hour or so. The supernatant peroxide had then become faintly green only, the mercury had become tarnished and pasty, and on opening the tube, a little nitric oxide escaped. The mercury was gradually converted into a white mass, sending out, in some experiments, slender branches with little globules of mercury borne on their points. Nitric oxide was continuously evolved, and the residual peroxide became olive-green. The white salt was gently warmed in a current of carbon dioxide for some time to evaporate unchanged peroxide. It was hard, and adhered firmly to the glass. Removed and ground to powder, it was found still to contain a little liquid peroxide. Tested, it proved to be mercurous nitrate, with some mercuric nitrate, but no nitrite. Tested by ferrous sulphate and by potassium iodide, only slight coloration was obtained, attributable to traces of nitric peroxide, which for some time adhered to it, in spite of exposure to air. In one experiment, in which both the mercury and the product of the action were weighed, but in which a very little metal remained in excess, the increase was found to be slightly greater than calculation for mercurous nitrate required, the excess in weight being, no doubt, caused by the mercuric nitrate found to be present. The reaction must have been, therefore, the replacement of nitrosyl by mercury—

$$2(NO)NO_3 + 2Hg = (HgNO_3)_2 + 2NO.$$

Action of Nitric Peroxide upon Silver.—Reduced spongy silver was used. It was sealed up with the peroxide in an atmosphere of carbon dioxide. The reaction proceeded very slowly. Nitric oxide was evolved, the excess of nitric peroxide became olive-green, but the silver did not appear to be much changed, even after several days' contact. This, however, seems to be due to the whiteness of the metal, which renders a thin coating of a white salt almost invisible, as an action did take place. The excess of peroxide, poured off from the silver and evaporated by itself, left no residue of silver salt. After drying the silver in a current of carbon dioxide, it was treated with water. This dissolved a considerable quantity of silver salt, although most of the metal had remained unattacked. The salt was nitrate, without admixture of nitrite. In the case of mercury, the action went on to the end in spite of the insolubility of the nitrate in the peroxide, because of the mobility of the metal, whilst in the case of silver, the solid metal became coated with nitrate, and the action was thus arrested. Nevertheless, we meet again with a reaction, which is the replacement of nitrosyl by the metal, and the conversion of nitrosyl nitrate into metal nitrate.*

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* Berthelot and Ogier (*Compt. rend.*, **96**, 30) speak of an action of "nitrous acid" upon hot silver in describing their experiments upon silver hyponitrite.

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Action of Nitric Peroxide upon Copper.—Reduced spongy copper was treated with nitric peroxide, in the same way as mercury and silver had been treated. Immediately on contact there was considerable action; brisk effervescence, through escape of nitric oxide, occurred at first and gradually lessened, and the copper turned grey, with a bluish or greenish tinge. The excess of peroxide became of an intense deep-green colour, unlike the dull olive-green in the mercury and silver experiments. This green liquid, decanted and partly evaporated, lost its green colour, and when the peroxide had all volatilised, nothing was left, so that the green colour was not due to dissolved copper salt. We are unable to explain the difference between copper and the other metals, in producing this colour. It was always observable. Perhaps the rapidity of the formation of nitric oxide by the copper had something to do with it. We should mention that the evolution of gas being so great, the point of the tube could not be sealed, as it had been in the experiments with the other metals, until action had considerably lessened. The green solution was, therefore, not due to any pressure upon the gas. In the mercury and silver experiments, in which the reaction takes place at the ordinary temperature, it is not strange that the nitric oxide should not combine with, or dissolve in (Armstrong) the nitric peroxide, to form the blue liquid which is produced at low temperatures.

Long digestion of the copper with the nitric peroxide did not seem to add much to the extent of the action, which at first proceeded so briskly. In one experiment, the copper was found to have taken up a fifth of its weight, but then the change of the copper is only on its surface. We believe the product of the reaction to be cuprous nitrate, mixed with a little cupric nitrate. Cuprous oxy-salts hardly exist, it is true, but we have here the absence of water as perhaps the reason why such a salt may be produced. Ground to fine powder and very gently warmed, so as to expel adhering nitric peroxide, it shows the following reactions. Aqueous vapour changes its colour to a red-brown; water at once changes it to a bright copper colour, evidently by formation of free copper. At the same time, the water becomes blue from the presence of cupric nitrate. This action of water, we interpret to be the decomposition of the grey cuprous nitrate into metallic copper and cupric nitrate. The action of water at once sets up an effervescence of nitric oxide from the copper, and basic copper nitrate is slowly produced. This action we regard as being one between finely divided—spongy and freshly precipitated—copper and cupric nitrate. If the first water is decanted, and the copper is washed, the latter no longer effervesces with water, but if the first blue-coloured solution be now poured back on the copper,

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effervescence begins again. Strong potassium hydroxide solution precipitates cuprous hydroxide with some cupric hydroxide, and leaves an azure-blue mother-liquor. Weaker alkali gives less cuprous hydroxide, and a free effervescence of nitric oxide. Strong sulphuric acid has no apparent effect, but the diluted acid acts much like water. On rendering the solution alkaline, an azure-blue mother-liquor is obtained. From the above reactions, it would seem that ammonia is formed during the decomposition of the substance by alkalis and acids. The filtered alkaline solution, obtained by treating the substance with potassium hydroxide, yields the reactions of nitrite to a small extent. But, since cuprous hydroxide seems in this case to have a reducing action upon the nitrate, producing ammonia and nitric oxide, this nitrite may be regarded as a secondary product.

The reaction of nitric peroxide with copper is of too uncertain a nature to throw light upon the constitution of the peroxide, at least until we know more about it.

Action of Nitric Peroxide upon Silver Nitrite.—Dry silver nitrite may be digested for days with nitric peroxide, and the latter may be repeatedly distilled off it, without its being oxidised, or in any way changed. This is a fact of importance in studying the effect of heat on silver nitrite, by which both nitric peroxide and silver nitrate are formed.

Action of Heat upon Silver Nitrite, Air being excluded.

By heating silver nitrite, Péligot obtained silver, nitric peroxide, and silver nitrate. One of us also re-investigated the effects of heat upon silver nitrite 14 years ago, and communicated an account of the results obtained to this Society. It was there shown that, by modifications in the way of heating, the products could be made to vary, nearly from nitric peroxide and silver only, to nitric oxide, silver, and silver nitrate. It was also proved that oxygen is absorbed from the air, and that nitric oxide acts as the carrier of this to form nitrate.

In that paper, it was assumed that the nitrate was formed by the oxidising action of the peroxide upon the nitrite. This assumption we now consider to be wrong, for reasons which we shall give after describing our recent experiments with silver nitrite. The object of these experiments was to test the effect of heating silver nitrite when not in contact with air.

Out of a piece of tubing, not more than 1 cm. in diameter, we constructed a horizontal retort with a receiver and gas-exit tube for connection with a Sprengel pump. After charging the retort with dried silver nitrite, its mouth was sealed off, the gas tube connected with the pump, and the apparatus exhausted, both retort and receiver being

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kept gently heated for some time to expel moisture. The receiver was then put into a mixture of ice and salt, and the flow of mercury stopped. The retort was next heated, by a large spirit flame, as rapidly as possible, and the nitrite thus decomposed in less than a minute. Much nitric peroxide condensed in the receiver, besides an abundant fume of silver nitrate, and the nitric oxide escaped at the exit-tube. Very little silver nitrate was carried over mechanically. The nitric peroxide had only a slight green colour, showing how easily, at a low temperature, nitric peroxide and nitric oxide may exist together without combining, and thus favouring Armstrong's belief in the non-existence of nitroysl oxide. Proceeding in this way, and weighing our nitric peroxide, we found it to represent not much less than two-thirds of the nitrogen of the nitrite, the rest of the nitrogen having become nitrate and nitric oxide. In the paper referred to, experiments are given in which the metallic silver obtained represented a much nearer approach to the production of only nitric peroxide and silver, but those experiments were conducted in hot air laden with steam. The mercury of the trough was only acted upon to a small extent, proving that very little nitric peroxide escaped with the relatively small volume of nitric oxide produced.

In another experiment, and in an apparatus very similar to that just described, silver nitrite was kept heated at 125° in absence of air for 15 hours, when gas had almost entirely ceased to come off. The mercury was considerably soiled by the gas, showing that nitric peroxide had been given off, but no liquid peroxide was ever condensed in the receiver, and very little red vapour was ever visible. In this way, nearly half the nitrite was converted to nitrate, as calculation requires, and the results in the paper referred to were thus confirmed.

We can now give our reasons for believing that the formation of silver nitrate is due to reaction between silver and nitric peroxide, and not between nitrite and the peroxide.

(1.) We have found, as already described in this paper, that nitric peroxide does act upon silver, and then forms nitrate and nitric oxide. (2.) We have found that nitric peroxide does not act upon silver nitrite in the least, even after prolonged contact. (3.) One of us has found that when silver nitrite was heated for 78 hours at a temperature slowly raised from 90° to 136° during that time, in an apparatus which allowed of the exit of gases and entrance of air occurring only through the space between the walls of a tube and a glass rod almost filling it, only a small fraction of the silver was obtained as metal, most of the nitrite having become a stable mixture or compound of nitrate and unchanged nitrite in molecular proportions. Now, whilst the conversion of nearly all even of the silver nitrite to nitrate, would in itself be consistent with either supposi-

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tion, the fact that so little metallic silver was found seems to indicate that the nitrate had been formed from the metal, and not directly from the nitrite. For if it had been the nitrite which was oxidising during the 78 hours' heating at 90—136°, then silver ought to have gone on increasing, as an effect of the continued action of heat upon silver nitrite, instead of being finally only 4⅓ per cent. of the whole silver, or 8⅓ per cent. of the silver of the changed nitrite. That it formed only this small proportion is due, we consider, to the silver being converted to nitrate nearly as fast as it was liberated from the nitrite. (4.) Facts seem to show that nitrites are non-oxylic salts, having, therefore, the metal united directly with the nitrogen. This is now widely admitted to be so in the case of silver nitrite, at any rate. On upholding this view of the constitution of nitrites in a recent paper to the Society, one of us has pointed out that it is apparently the metal radical which is oxidised when oxidation takes place. The conversion of nitrite to nitrate, on this view, involves the oxidation of the metal, and it seems improbable to us that silver and nitrogen in nitrite part from each other to take in oxygen. At least, silver sulphide does not oxidise to silver sulphate, but readily changes with hot water to silver itself and sulphuric acid, and in an experiment given in a paper by one of us already referred to, most of the silver of the silver nitrite was got in the metallic state by the action of hot air and steam. These are our reasons for believing that the nitrate formed, when silver nitrite is heated, comes not from the oxidation of the nitrite, but from a reaction between silver and nitric peroxide (nitrosyl nitrate).