LXXVI.—*A Product of the Action of Nitric Oxide on Sodium Ethylate.*

By G. W. MACDONALD, B.Sc., and ORME MASSON, M.A., D.Sc.

THE perusal of W. Traube's paper, "Ueber Isonitramine,"* has led us to decide on the publication of such results as we have already obtained in the study of the above interaction, though they are incomplete, and we should otherwise have waited till we had obtained fuller and more satisfactory analytical data, and had succeeded in clearing up certain doubtful points.

We have found that nitric oxide is absorbed in large quantity, though but slowly, by an alcoholic solution of sodium ethoxide, and that the most characteristic product of the change is the sodium salt of a new acid, which, being insoluble in alcohol, separates as a crystalline precipitate. From the sodium compound various other salts have been made, and the unstable acid has been obtained in aqueous solution. Analyses of the copper salt point to $\text{CH}_2\cdot\text{N}_4\text{O}_4\text{H}_2$ as the formula of the acid, half the hydrogen of which is replaceable by metal. This formula is identical with that which we now find accorded by Traube (who bases it on the analysis of a barium salt) to a compound which he designates *methylene-diisonitramine*, $\text{CH}_2(\text{N}_2\text{O}_2\text{H})_2$. He obtained the sodium salt, together with sodium acetate, by the action of nitric oxide on acetone in the presence of alcoholic soda, and he states that the action occurs according to the equation

As the compounds obtained by us and those described by Traube agree not only in composition but also, so far as we can judge from his account, in their characteristic properties, there can be no doubt that they are identical. In that case, it would appear probable,

* *Berichte*, 1894, p. 1507. This number, issued on the 25th June, was received in Melbourne on the 2nd August. The results of our work, now described, were all obtained before that date.—O.M., 6th August, 1894.

either that the acetone employed by Traube is not an essential participator in the action, or that in our apparently simpler mode of preparation acetone or some similar compound is produced as a preliminary step. We have, however, given but little attention as yet to the products of the action other than the new sodium salt, this being an aspect of the question which we had set aside in the meantime.

Mode of Action.—The first experiments were undertaken in order to ascertain whether nitric oxide would react with sodium amalgam in presence of absolute alcohol to produce sodium hyponitrite, this salt having recently been shown by Jackson (Proc., 1893-94, No. 128, p. 210) to be insoluble in, and stable in the presence of, alcohol, though it is decomposed by water. Hyponitrite was not obtained except in certain cases where the complete exclusion of air was somewhat uncertain; but in all other cases a white or yellowish crystalline precipitate was formed, which had peculiar properties, and could not be identified with any known substance. This led to the trial of an alcoholic solution of sodium ethoxide, instead of sodium amalgam and alcohol, and resulted in the production of the same precipitate as before.

If the nitric oxide and excess of the ethoxide be enclosed in a eudiometer tube over mercury, the absorption of the gas can be observed, and is found to go on slowly, and with great regularity, till at the end of about a fortnight it is complete. During this time, the crystalline precipitate, which is at first white, increases in quantity and acquires a decided yellow tint, as does also the alcohol. The development of colour is similar to, but not so pronounced as, that seen in the case of sodium ethoxide solution exposed to air. In one such experiment, 6.2 c.c. of a solution of the ethoxide containing 0.237 gram of sodium was put up with 61.7 c.c. (at normal pressure and temperature) of nitric oxide, that is, the ratio of Na to NO was about 4 : 1; and in another experiment the ratio taken was 6 : 1. In both these cases, the appearances were those described above, and the absorption became complete in about 13 days, only a very small volume of what appeared to be nitrogen remaining, equal to about 3 per cent. of the original gas. This, however, was not impurity derived from the nitric oxide used, which had been prepared with special care, and proved to be pure to the extent of 99.8 per cent. In another experiment, in which the ratio Na : NO was made unity, the absorption is not yet complete, nor has it altogether stopped, although almost three months have elapsed since it was started; in this case, both the crystalline precipitate and the alcohol are quite devoid of colour.

In order to obtain larger quantities of the salt, a glass gas-holder was used, capable of holding about 5 litres. A known quantity of the

ethoxide solution was poured in so as to form a layer at the bottom, and the air was then displaced by dry hydrogen, and this in turn by pure nitric oxide. This gas-holder was put in connection, through a drying tube, with another and similar gas-holder full of nitric oxide, on which a constant water pressure could be maintained. Special care was taken to exclude air at the outset, and to guard against leakage through the taps. After two or three weeks, when several litres of the gas had been absorbed, the residual nitric oxide was displaced by hydrogen, and the gas-holder then opened. The crystalline precipitate was then separated from the excess of ethoxide and from any soluble products, by filtration and thorough washing with alcohol, but it was not found possible to entirely free it from colouring matter in this way. It can, however, be dissolved in water and reprecipitated by alcohol; and if the alcohol is allowed to diffuse slowly into the aqueous solution large plates and long delicate needles are obtained. From the sodium salt, certain insoluble metallic salts have been prepared, which may be described before proceeding further.

The copper salt is the most characteristic, and its formation is a delicate test for the presence of the sodium, or other soluble, salt in solution. It separates as a sky-blue powder when copper sulphate is added, not in excess, to a solution of the sodium salt slightly acidified with acetic or sulphuric acid. It is completely insoluble in water, cold or hot, and is but slightly affected by cold dilute acids, except nitric acid, which attacks it readily; it dissolves in excess of copper sulphate, however, forming a green solution, whilst with ammonia it gives a dark blue solution, from which it may be reprecipitated by neutralisation. The dry salt, when heated, decomposes with so much energy as to produce glowing and to scatter the resulting cupric oxide. Four different preparations were used for analysis, of which I, II, and III were got from the earlier experiments with sodium amalgam, and IV by the sodium ethoxide method. The salt was in all cases dried over sulphuric acid. The discrepancies in the results obtained are somewhat greater than could be desired, but they leave little room for doubt as to the correctness of the formula $\text{CH}_2\text{N}_4\text{O}_4\text{Cu}$ for the pure salt.

		Found.			
	Calculated for $\text{CH}_2\text{N}_4\text{O}_4\text{Cu}$.	I.	II.	III.	IV.
C	6.07	—	6.19	6.23	6.89
H	1.01	—	1.35	1.42	1.56
N	28.35	—	27.43	—	26.00
O	32.42	—	—	—	—
Cu	32.15	31.46	31.21	31.93	31.07

The cadmium salt falls rather slowly as a white, crystalline precipi-

tate of characteristic appearance, when cadmium sulphate is added to an aqueous solution of the sodium salt. In its behaviour towards acids, and on heating, it resembles the copper salt. It is a hydrated compound, and estimations of the cadmium in samples obtained from two different preparations of the sodium salt and dried over sulphuric acid are in accordance with the formula $\text{CH}_2\text{N}_4\text{O}_4\text{Cd}, 2\text{H}_2\text{O}$. This formula requires 39.72 per cent. of cadmium; found, 40.03, 39.50, and 40.22 per cent. Further analyses of this salt have not yet been made.

The silver salt is a white, curdy precipitate, somewhat soluble in cold water, and readily dissolved by dilute acids or ammonia, but can be re-obtained from such solutions by exact neutralisation. It darkens slowly in the cold, and when boiled with water it decomposes rapidly with evolution of gas and deposition of a silver mirror. It explodes when heated in the dry state. A single estimation of silver in a sample partially decomposed by exposure gave 63.22 per cent.; calculated for $\text{CH}_2\text{N}_4\text{O}_4\text{Ag}_2$, 61.71 per cent.

The barium salt, obtained by precipitation with barium chloride, has properties agreeing, so far as we have observed them, with those described by Traube (*loc. cit.*). He gives the formula

for the salt dried over sulphuric acid. His description of the silver salt (the only other salt examined by him) also agrees with our observations.

Other characteristic insoluble salts are obtained by precipitating a solution of the sodium salt by calcium chloride, lead acetate, mercurous nitrate, and ferrous sulphate.

The sodium salt itself has not, as yet, been fully examined. As stated above, it is obtained in the first instance, after washing the product with alcohol and drying over sulphuric acid, as a crystalline powder, more or less yellow from the presence of impurity. It is freely soluble in water, but does not deliquesce or alter on exposure to air. It explodes violently when heated. Estimations of the sodium and nitrogen contained in different preparations, not quite pure, point to the ratio Na:2N, and to the formula $\text{CH}_2\text{N}_4\text{O}_4\text{Na}_2, \text{H}_2\text{O}$. This requires 23.23 per cent. of sodium and 28.28 per cent. of nitrogen; and the results obtained were

Sodium, (I) 23.22, (II) 23.37, (III) 23.51 per cent.

Nitrogen, „ 26.84, „ 26.77, „ 26.36 „

The large crystals already mentioned as obtained by diffusion of alcohol into the aqueous solution appear to be a different hydrate, but have not been analysed. They lose water at about 150°C , leaving

an anhydrous salt with otherwise unaltered chemical properties. Explosion occurs above 200° . The aqueous solution of the salt is faintly alkaline to litmus. It is decomposed by sulphuric acid with evolution of gas which contains nitrous and nitric oxides, and nitrogen; this decomposition is rapid if strong acid is employed or if heat is applied, but with cold dilute sulphuric acid the action is slower and a peculiar odour is noticeable. The salt gives the Liebermann reaction with phenol and strong sulphuric acid. It readily reduces acid potassium permanganate, but not Fehling's solution. It reduces gold chloride even in the cold, and platinum chloride on prolonged boiling. It decolorises iodine solution.

The ammonium salt has been obtained by decomposing the copper salt, suspended in water, with a slight excess of ammonium sulphide, filtering, and evaporating on the water-bath. Partial decomposition occurs, but a crystalline residue is obtained which contains ammonia and gives all the precipitations already mentioned as characteristic of the sodium salt. It does not explode when heated, but decomposes with evolution of gas.

The free acid has also been obtained, though only in solution, from the copper salt by suspending it in water and passing in a stream of hydrogen sulphide. The excess of the latter is then removed by a current of hydrogen, which also serves to coagulate the copper sulphide and make filtration possible; the solution obtained in this way is strongly acid to litmus, and reduces potassium permanganate solution. When fresh, it can be reconverted into the sky-blue copper salt by precipitation with copper sulphate, or into the sodium salt by neutralising with soda and precipitating with alcohol. There can thus be no doubt that the solution, when first prepared, contains the acid $\text{CH}_2\text{N}_4\text{O}_4\text{H}_2$. But it is rapidly decomposed when heated; and, even in the cold, it slowly evolves gas, apparently nitrous oxide and a small amount of nitric oxide, and a yellow solution remains which contains a different acid and gives different reactions. After some days, it no longer gives the characteristic copper precipitate; it yields a solid residue on evaporation; with alkalis, it gives deep orange-coloured solutions; and with silver nitrate, it gives a salt which separates from boiling water in the form of beautiful, red crystals, insoluble in cold water, and highly explosive when heated. Further examination of the free acid and its decomposition products has not yet been possible.

Constitution of the Acid.—Among compounds already known, those which approach nearest to the new acid and its salts in mode of formation and in properties are, as Traube also notices, Frankland's so-called dinitromethylates and dinitroethylates (*Phil. Trans.*, **147**, 59). These salts differ from ours in being all soluble in water, but

they resemble them in their explosive characters and in other respects, and especially in their mode of decomposition by acids. It is therefore probable that their constitution is similar, the new compound differing from Frankland's only in so far as it contains the dyad methylene group in place of monad alkyl.

The constitution of the $-\text{N}_2\text{O}_2\text{H}$ -group requires further investigation, but some evidence is already available. Franchimont and van Erp (Abstr., 1894, i. 273) have quite recently shown (contrary to the view suggested in the new edition of *Watts' Dictionary*) that this group in Frankland's compounds must be isomeric, and not identical with that contained in the nitramines, which do not decompose under the influence of dilute sulphuric acid. It is on this account that Traube applies the name *methylenediisonitramine* to the new compound, implying thereby that it contains a group isomeric with the nitramine group $-\text{NH}\cdot\text{NO}_2$, but leaving the question of the exact constitution unanswered. The choice seems to lie between the alternatives $-\text{N}\cdot\text{N}\cdot\text{OH}$ and $-\text{N}<\overset{\text{NO}}{\underset{\text{O}}{\text{OH}}}$. Of these, the former was suggested

by Frankland himself in his account of the dinitroethylates, but no sufficient reasons were given in support of it. Either formula is capable of expressing the production of nitrous oxide by decomposition of the salts with acids and the formation, in the case of the new methylene compound, of a strong reducing agent, namely, formaldehyde, capable of reducing gold and silver salts, and potassium permanganate. But the second formula is better in accord with the fact now observed that the new sodium salt gives the Liebermann reaction, which is generally accepted as evidence of the presence of a nitrosyl group, and is here strongly suggestive of a nitrosamine. According to this view, which seems the most likely one in the present state of our knowledge, the new compound *methylenedihydroxynitrosamine*, $\text{CH}_2[\text{N}(\text{NO})\cdot\text{OH}]_2$.

*The Chemical Laboratory,
University of Melbourne.*