XXXII.—*The Nitroprussides.*

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THE nitroprussides have allured me for years by the beauty of their reaction with soluble sulphides, and also because there is an evident uncertainty about their composition. They are evidently formed on the type of the ferridcyanides. Thus :

The only doubtful question seems to be *what* oxide of nitrogen replaces the MCy. A mere glance at Playfair's most laborious and careful ultimate analyses showed the hopelessness of endeavouring to gain light in this way by improving on them. The only conclusive proof, it was felt, would be the actual formation of nitroprusside from ferridcyanide by the displacement of an atom of alkaline cyanide by one of the oxides of nitrogen. Protoxide of nitrogen, NO, being generally rejected in published formulæ, was not tried; but as Gerhardt and almost all other chemists represent it as the binoxide NO₂, an apparatus was fitted up as follows, for the purpose of testing the correctness of this view :—

The flask C has a solution of pure ferridcyanide acidulated with sulphuric acid and kept hot, so that the binoxide NO₂, instead of having to displace MCy, has the far easier work of displacing HCy, if it can. The whole apparatus was first filled with car-

bonic acid to expel oxygen, and pure nitric oxide (NO_2) from A, washed from any nitrous acid in B, was then passed in for some time. Flask C by degrees became very blue and muddy, and when, after an hour, the contents were examined, *no trace* of nitroprusside was found.

The operation was then exactly repeated, only that instead of pure nitric oxide the red nitrous acid vapours from starch and nitric acid were passed in. The difference was wonderful; *no* Prussian blue appeared in flask C. The colour changed rapidly to the red of nitroprusside, and much hydrocyanic acid came off into D; and on opening the flask all ferridcyanide of potassium had disappeared, the conversion to nitroprusside being almost perfect. Since then I have never had a doubt but that the generally received formula $\text{Fe}_2\text{Cy}_5\text{NO}_2\text{Na}_2$ was wrong, and that the true formula has NO_3 or NO_4 instead, but which, the last experiment does not determine, for NO_3 from starch always has NO_4 mixed with it. The presence of NO_3 or NO_4 as the nitrogen-oxide essential to nitroprusside, is further shown by a very simple experiment—the reverse of the last. On adding to a solution of pure nitroprusside a solution of potash and some prussic acid, and warming, the red of the nitroprusside changes for an instant to deep yellow, and then to pale yellow. The solution will be found to contain ferridcyanide, with plenty of nitrite, but no trace of nitroprusside. Here NO_3 or NO_4 has been displaced by KC_y , and ferridcyanide reproduced.

I felt that nothing could be conclusive but the actual displacement of an alkaline cyanide in ferridcyanide by pure NO_3 , which can be obtained by the action of acetic acid on an alkaline nitrite, which mixture absolutely excludes NO_4 . After trying many methods for displacing KC_y in ferridcyanide of potassium, the following experiment was tried with perfect success:—Ferridcyanide of potassium solution was mixed with a solution of corrosive sublimate and acetic acid, and a nitrite added, and the whole was left for some hours, when, on examining the mixture, nitroprusside was found in abundance, which experiment conclusively stamped NO_3 as the oxide. The reaction was as follows:—

Nitroprusside.

and the true formula of the sodium-salt is

The fact of this being the true formula is further confirmed by the close correspondence between the percentage of each of the elements calculated from this formula and Playfair's own numbers, which is closer than the numbers derived from Gerhardt's formula.

	Calc. from NO ₃ formula.	Playfair's.	Gerhardt's NO ₂ formula.
C	= 19·6	19·5	20·1
N	= 27·5	27·8	28·1
Fe	= 18·3	19·3	18·8
Na	= 15·0	15·2	15·4
H	= 1·3	1·3	1·3
O	= 18·3	—	16·3
	<hr/> 100·0		<hr/> 100·0

The success of this reaction on the small scale suggested it as a means of manufacturing nitroprusside on the large scale. The present retail price of the sodium-salt, 6s. per oz., or £4 16s. per lb., while the ferrocyanide from which it is derived is worth about 1s. 6d. per lb., sufficiently shows the difficulties attending the present method.

After very many experiments the following method has been arrived at, which, though by no means perfect, will furnish nitroprusside of sodium by the pound without difficulty.

1. A strong solution of caustic soda is prepared, and thoroughly saturated with the nitrous acid vapours from starch and nitric acid (old battery acid does well). The amount of true nitrite of soda, NaONO₃, in this solution is determined by permanganate by taking a small measured quantity, diluting largely with water, acidifying with sulphuric acid, and observing the amount of standard permanganate decolorised. Fe₄ = NaO.NO₃ in decolorising power. The amount of real nitrite of soda in the solution being known, is recorded on the bottle.

A mixture of any bulk is then made in the following proportions :—

A {	Ferridcyanide of potassium	332 grs.	} in $\frac{1}{2}$ pint of boiling water,
	Acetic acid (Beaufoy's) ..	800 grs.	
B {	Corrosive sublimate ..	164 grs.	} make up to $\frac{1}{2}$ pint with cold water,
	Solution of nitrite soda =	80 grs. of true NaONO ₃	

adding acetic acid, if necessary, until quite clear. Pour the cold solution B into the hot solution A. The mixture becomes at

first turbid, but in a few minutes afterwards quite transparent. It should be kept at a temperature of 140° (at which point little nitrous acid is lost) for some hours, with addition, if necessary, of more nitrite of soda and acetic acid from time to time, until all ferridcyanide has disappeared. When this is the case, the whole mixture may be boiled down, until, on cooling, it solidifies to a thick paste. The right state of concentration has been attained, when on beating the paste up, and squeezing in linen, a *pale* syrup, chiefly of acetate of potash, is expressed. The pearly-looking mass freed from acetate of potash, as far as possible, must be redissolved in such an amount of boiling water, that on cooling a large proportion of cyanide of mercury separates in white pearly scales, quite free from nitroprusside crystals. On squeezing in linen, a deep-red solution of nitroprusside is expressed, and a white, pearly mass of cyanide of mercury remains on the linen. On concentrating the red filtrate, a large crop of crystals of nitroprusside of sodium is obtained in a mother-liquid containing more or less cyanide of mercury, in pearly scales, easily separated by throwing the whole on a moderately coarse hair sieve, which will retain the prisms of nitroprussides of sodium, and allow the cyanide of mercury to pass through. The prisms may be washed quite clean by allowing the cyanide of mercury to settle down in the filtrate, and using the clear supernatant fluid for washing. The operation can, of course, be continued as far as it may be deemed profitable. If the cyanide of mercury is not wanted as such, it can be made to furnish hydrocyanic acid and corrosive sublimate for use again, by boiling with hydrochloric acid.

It may be added, in conclusion, that nitroprussides react well only with monosulphides. The more of a persulphide the solution contains, and the deeper the yellow colour, the less distinct is the reaction. This difficulty can be overcome by warming the yellow persulphide with sufficient cyanide of potassium to decolorise it, when the beautiful carmine of the monosulphide will be obtained.