

CLXIX.—*The Constitution of the Nitroprussides.*
Part II. The Alkylation of Nitroprussic Acid.

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In a previous communication (T., 1919, **115**, 1429), it was shown that nitroprussides were derived from an acid of the molecular formula $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$. The series of conductivity measurements described in the same paper has now been completed by a measurement of the conductivity of tetramethylammonium nitroprusside. Measurements of the conductivity of nitroprussic acid itself have been made, and indicate that the acid is stronger than sulphuric acid.

In addition, experiments have been carried out on the alkylation of nitroprussic acid, as a result of which diethyl nitroprusside has been isolated.

EXPERIMENTAL.

Tetramethylammonium Nitroprusside, $(\text{Me}_4\text{N})_2[\text{Fe}(\text{CN})_5\text{NO}]$.

This salt was prepared by treating the silver salt with the calculated quantity of tetramethylammonium iodide in aqueous

solution, the filtrate from silver iodide being evaporated under diminished pressure, and the residue crystallised from alcohol. The salt forms reddish-brown leaflets, which are very soluble in water (Found : Fe = 15.3. $C_5ON_6Fe(NMe_4)_2$ requires Fe = 15.4 per cent.).

Conductivity measurements.

ν .	μ .	α .
16	129.1	0.62
32	147.8	0.70
64	162.1	0.77
128	176.5	0.84
256	189.6	0.90
512	198.1	0.94
1024	205.5	0.98
∞	210	—

The comparison of these results with those previously obtained (*loc. cit.*) is of interest :

Cation.	μ_{32} .	μ_{∞} .	α_{32} .
NH_4	218.0	268.0	0.82
$MeNH_3$	185.2	240.0	0.77
Me_2NH_2	172.1	230.0	0.75
Me_3NH	154.0	212.0	0.73
Me_4N	147.8	210.0	0.70

Nitroprussic Acid, $H_2[Fe(CN)_5NO]$.

This acid was prepared by treating an aqueous solution of the barium salt with the calculated quantity of sulphuric acid, and evaporating the filtrate from barium sulphate under diminished pressure. In this way, the acid was obtained as reddish-brown leaflets, very soluble in water, giving an unstable solution (Found : Fe = 26.2. $C_5H_2ON_6Fe$ requires Fe = 25.7 per cent.).

The conductivities of various preparations were determined. The results were not entirely satisfactory, and only approximate figures could be quoted for the actual conductivity at particular dilutions. From each series of determinations, however, it was found that, in *N*/20-solution, nitroprussic acid is dissociated to the extent of about 85 per cent., and is accordingly of the same order of strength as benzenesulphonic acid.

Nitroprussic acid combines readily in aqueous solution with organic bases. Thus, the *pyridine* salt forms red needles (from alcohol) [Found : Fe = 13.0; H_2O = 12.6. $C_5ON_6Fe.(C_5H_5NH)_2.3H_2O$ requires Fe = 13.0; H_2O = 12.6 per cent.]. The *benzidine* salt is a well-defined, sparingly soluble, scarlet solid.

The Alkylation of Nitroprussic Acid.

Methyl iodide was heated in alcoholic solution, under reflux, with silver nitroprusside. A pronounced odour of isonitrile was developed, and the filtrate from silver iodide, on evaporation under diminished pressure, gave a red, hygroscopic, lachrymatory substance, which was almost certainly dimethyl nitroprusside, but it decomposed on drying, more particularly under the action of light.

A similar experiment with ethyl iodide afforded well-defined, red prisms of diethyl nitroprusside (Found : Fe = 20.0. $C_9H_{10}ON_6Fe$ requires Fe = 20.4 per cent.). The compound gives the usual reactions of a nitroprusside, and on the straightforward evidence would appear to have the formula $Et_2[Fe(CN)_5NO]$. A molecular-weight determination in water (the only cryoscopic solvent dissolving the compound) gave $M = 83, 89$ (two determinations). The above empirical formula requires $M = 274$, and it is therefore evident that diethyl nitroprusside is hydrolysed in aqueous solution to give ethyl alcohol and nitroprussic acid.

From the fact that isonitriles are invariably formed when alkyl iodides interact with complex cyanogen compounds, it seems probable that in many of these compounds, if not in all, some of the groups written as cyanogen are in reality *isocyanogen* groups. This would afford an explanation of certain cases of isomerism, as, for example, that of the methyl ferrocyanides and cobalticyanides (Hartley, T., 1914, **105**, 521, etc.), since such isomerism may evidently be due to a difference in structure of the cyanogen radicles in the molecule, even if one adopts the simple co-ordination theory.

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[Received, August 8th, 1921.]