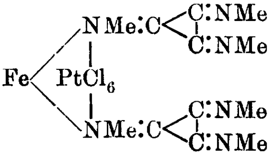
LXXIV.—*The Alkylation of the Ferro- and Ferri-cyanides.*

By Ernald George Justinian Hartley.

In two recent communications (Trans., 1910, **97**, 1066, 1725) the author described some new derivatives of hydroferrocyanic acid formed by the action of anhydrous potassium ferrocyanide on methyl sulphate. There were thus obtained several salts of a base, $(CH_3)_6FeC_6N_6(OH)_2$, which was too unstable to exist in the free state; for example, the acid sulphate had the composition $(CH_3)_6FeC_6N_6SO_4,H_2SO_4$. From the latter was prepared, amongst other derivatives, a characteristic insoluble platinichloride, which was found to be most useful for identifying these salts. Finally, tetramethyl ferrocyanide was obtained. In a subsequent paper on the constitution of these compounds (Trans., 1911, **99**, 1549) it was shown that the methyl groups are all directly attached to nitrogen, and a formula similar to that suggested by Browning (Trans., 1900, **77**, 1238) was adopted to represent their constitution, thus:



for the platinichloride.

It was thought interesting to ascertain whether ferricyanides would behave in a similar way, and experiments were carried out exactly as before, but substituting potassium ferricyanide for the ferrocyanide. The former reacted with methyl sulphate at 100° with much decomposition, a large quantity of some compound of the nature of Prussian blue being formed. On filtering the liquid portion of the mixture from the solid matter and distilling off the excess of methyl sulphate under diminished pressure, a crystalline residue was left, which proved to be exactly the same as that produced when the ferrocyanide was used, namely, a mixture of the above-mentioned acid sulphate and the neutral methosulphate, $(CH_3)_6FeC_6N_6(SO_4{\cdot}CH_3)_2$.

It is evident, therefore, that under these conditions some reducing action takes place, and that it is not possible in this way to obtain a methylated ferricyanogen derivative. Owing, however, to the extremely poisonous properties of methyl sulphate, no further experiments were made to determine the exact nature of the reduction.

The reaction between alkyl iodides and silver ferro- and ferri-cyanides was next investigated. Freund (*Ber.*, 1888, **21**, 931) first prepared tetraethyl ferrocyanide by this method, but he gives no details as to the amount of product. Browning (*loc. cit.*) repeated his experiments, and states that he obtained a very bad yield, a result which the author has also experienced when the preparation was carried out as far as possible according to Freund's paper. Since it appears that a reaction of this nature should take place fairly completely, a further study of the process was undertaken. The substances used for the first experiments were silver ferrocyanide and methyl iodide with a view to obtain tetramethyl ferrocyanide, since the properties of the methylated ferrocyanogen derivatives were more familiar to the author than those of the corresponding ethyl compounds. Five grams of dry powdered silver ferrocyanide were heated with 10 c.c. methyl iodide in a sealed tube at about 95° for six hours. On cooling it was seen that the solid matter had altered in appearances, and consisted largely of a grey, crystalline powder. The excess of methyl iodide was filtered off, and on evaporation left only a trace of a dark brown substance. The solid crystalline portion when dried weighed 11·4 grams, which corresponds very closely with an addition of six molecules of methyl iodide to each molecule of silver ferrocyanide. Since a previous experiment had shown that tetramethyl ferrocyanide combines very readily with methyl iodide to form hexamethylferrocyanogen iodide, $(CH_3)_6FeC_6N_6I_2$, when the two are heated together in a sealed tube as above, it was at first concluded that silver iodide and this hexamethylated compound had been produced in this case. The crystalline matter was therefore first digested with chloroform in order to dissolve any of the tetramethyl compound, if present, when only a very small amount of the above brown substance was extracted; afterwards it was heated with methyl alcohol, which has been found to dissolve hexamethylferrocyanogen iodide quite readily. In this case, however, only a further small quantity of the same brown-coloured matter was removed.*

It thus seemed probable that the substance was a compound of silver iodide with hexamethylferrocyanogen iodide, especially as it appeared under the microscope to consist of a homogeneous crystalline powder. This was subsequently confirmed, when it was found that the double salt is decomposed by digestion with warm dilute

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* This brown substance, of which only a fraction of a gram was formed, contained iron, carbon, nitrogen, and iodine. It is identical in its properties with the dark crystalline compound described later in this paper in the section on ferricyanides.

nitric acid into silver iodide and hexamethylferrocyanogen nitrate; for example, in one experiment 2·120 grams were gently warmed with nitric acid until the insoluble matter had become entirely yellow. The silver iodide when washed and dried weighed 1·350 grams, the calculated amount being 1·331 grams, assuming the double salt to be $(CH_3)_6FeC_6N_6I_2,4AgI$. In some experiments where the reaction had not been so complete, some unchanged silver ferrocyanide could be seen mixed with the silver iodide. On evaporating the filtrate from the silver iodide to dryness, a crystalline mass was left. This was dissolved in ethyl alcohol, and to the solution concentrated sulphuric acid was added, when an acid sulphate was precipitated the identity of which as a hexamethylferrocyanogen salt was definitely confirmed by a microscopic examination of the platinichloride.

A second method of decomposing the double salt consists in digesting it with a warm solution of silver nitrate, when the same nitrate as above passes into solution, and the silver iodide is all separated according to the equation:

$$(CH_3)_6FeC_6N_6I_2,4AgI + 2AgNO_3 = (CH_3)_6FeC_6N_6(NO_3)_2 + 6AgI.$$

In carrying out the above reaction between silver ferrocyanide and methyl iodide, a large excess of the latter was used in order that the silver salt should be completely covered with liquid. Some experiments were subsequently made, in which the proportion of methyl iodide to the silver salt was rather less than four molecules to one, and the former was mixed with an indifferent solvent (ethyl alcohol and carbon tetrachloride), so as to bring it in contact with the salt, but in neither case was any trace of tetramethyl ferrocyanide found, although when ethyl alcohol was employed the reaction was somewhat complicated, a considerable amount of hydrocyanic acid being produced and a double cyanide of hexamethylferrocyanogen and silver, soluble in chloroform, was isolated in small quantity. In the main, however, the reaction appeared to be the same as when excess of methyl iodide was taken, but, of course, in this case a considerable proportion of the silver ferrocyanide was unacted on.

The reaction between silver ferricyanide and methyl iodide was next investigated. 3·05 Grams of the silver salt were heated with 7 c.c. of methyl iodide for seven hours at 95° in a sealed tube. The solid matter had thereby been converted into a crystalline powder very similar to that formed when the ferrocyanide was used, but in addition to the grey crystals there were seen to be numerous dark brown plates and needles, many with an iodine-like lustre. After filtering and drying, the solid portion weighed 7·51 grams, which again corresponds with an addition of nearly six molecules of methyl iodide to each molecule of the silver salt. The brown crystals were found to be only sparingly soluble in alcohol, but very soluble in hot acetone. The whole of the solid matter was therefore extracted with this solvent, when a dark brown solution was obtained, which deposited the substance in almost black crystals on evaporation. The total amount of this substance, including the part extracted with alcohol and a small quantity left on evaporation of the excess of methyl iodide, was 1·24 grams. The portion of solid matter insoluble in acetone now appeared under the microscope to consist of homogeneous crystals. When treated either with nitric acid or silver nitrate in the same way as the previously described ferrocyanide, this salt also was decomposed into silver iodide and a crystalline nitrate, which proved to be the same as that obtained from the ferrocyanide, namely, hexamethylferrocyanogen nitrate. This was confirmed by conversion of the nitrate into the acid sulphate, in which the iron and SO_4 were determined (Found, Fe = 11·11 and 11·42. Calc., Fe = 11·23; SO_4 = 38·24. Calc., 38·68 per cent.), and into the characteristic platinichloride.

2·188 Grams of the double salt after digestion with dilute nitric acid gave 1·385 grams of silver iodide, which corresponds with the formula $(CH_3)_6FeC_6N_6I_2,4AgI$, the calculated amount being 1·374 grams.

The dark crystalline substance deposited from acetone was next examined. It was slightly contaminated with some oily matter, from which it was not found possible to free it entirely. It loses no weight at 100°, but on further heating it evolves iodine, and on strong ignition leaves a residue of ferric oxide, but no silver. When boiled with potassium hydroxide an alkaline vapour is evolved, accompanied by a strong odour of *iso*cyanides. It contains no free iodine, since it is altogether insoluble in carbon tetrachloride, and only sparingly so in chloroform or alcohol, forming a brown solution in both cases. It is insoluble in water, but on treatment with a solution of silver nitrate it is rapidly decomposed, even in the cold, a strongly acid solution resulting, and a mixture of silver iodide and iodate being precipitated. On filtering and removing the excess of silver with hydrochloric acid and evaporating to dryness, a crystalline residue is left, which is soluble in alcohol. A few drops of concentrated sulphuric acid added to this solution produce a crystalline precipitate, which can be identified as a hexamethylferrocyanogen salt by conversion into the platinichloride. These properties show pretty conclusively that the substance is a hexamethylferrocyanogen periodide, in which a part of the iodine is somewhat loosely held and reacts with silver nitrate in the same way as free iodine, forming silver iodide and iodate and nitric acid. A determination of iodine agrees fairly well with the number required for the formula $(CH_3)_6FeC_6N_6I_6$, considering that the substance could not be obtained in a perfectly pure condition:

0·2274 gave 0·2918 AgI. I=69·3.

$C_{12}H_{18}N_6I_6Fe$ requires I=71·5 per cent.

In order to verify the composition of this compound, a small quantity was prepared synthetically. 0·32 Gram of pure tetramethyl ferrocyanide was heated with excess (0·7 gram) of iodine and 4 c.c. of methyl iodide in a sealed tube at 105° for six hours. On cooling it was seen that the solid matter consisted entirely of dark crystals, completely resembling the above periodide, both in appearance and properties. After washing away the excess of iodine with carbon tetrachloride, the crystals weighed 1·23 grams, the calculated weight, assuming the above formula, being 1·25 grams.

A determination of the iron and iodine gave the following numbers:

0·4741 gave 0·0363 Fe_2O_3. Fe=5·36.
0·2551 „ 0·3373 AgI. I=71·4.
$C_{12}H_{18}N_6I_6Fe$ requires Fe=5·27; I=71·5 per cent.

The reaction between silver ferricyanide and methyl iodide can now be expressed by the following equations:

$$\text{(i)}\quad Ag_3FeC_6N_6 + 6CH_3I = (CH_3)_6FeC_6N_6I_2 + 3AgI + I.$$

The ferricyanide is here reduced to ferrocyanide by the methyl iodide with liberation of iodine. The hexamethylferrocyanogen iodide then combines partly with the silver iodide and partly with the free iodine, and the complete equation can be written:

$$\text{(ii)}\quad 4Ag_3FeC_6N_6 + 24CH_3I = 3(CH_3)_6FeC_6N_6I_2,4AgI + (CH_3)_6FeC_6N_6I_6.$$

It would appear probable from these experiments that ferricyanogen derivatives similar to the methylated ferrocyanogen compounds cannot be obtained, and since the production of such alkylated ferricyanides was the main object of this research, it was not considered worth while to carry on this work much further. It may, however, be mentioned that one or two experiments carried out with silver ferrocyanide and ethyl iodide show that under similar conditions the reaction is not so complete as with methyl iodide. A small quantity of tetraethyl ferrocyanide was usually formed, and also a double silver salt, the properties of which resembled those of the corresponding methyl compound.

Preliminary experiments on the reaction between silver cobalticyanide and methyl iodide show that this salt behaves quite differently from the ferricyanide. It is hoped that it will shortly be possible to lay these results before the Society.

This work has been carried out in Lord Berkeley's laboratory, to whom the author's best thanks are due.

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