# CIV.—*The Action of Cuprous Cyanide on Methyl Iodide.*

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In a previous paper (J., 1916, **109**, 1296) the author showed that silver cyanide and methyl iodide combine to give two compounds, $(AgNC)_2$,MeI and AgNC,MeI, according to the temperature of the reaction.

Similar experiments with methyl iodide and cuprous cyanide (for preparation of the latter, see Bassett and Corbet, J., 1924, **125**, 1667) have been carried out with the following results.

At the boiling point of methyl iodide very little combination takes place. When the mixture is heated at 100° in a sealed tube for several hours, a *substance* is formed which has the composition $(CuNC)_3$,MeI. This is a white, microcrystalline powder which can be dried in the air without decomposition, but is unstable, gradually losing methyl iodide, when placed under reduced pressure. On heating to 100°, the cuprous cyanide is recovered almost unchanged.

When the substance is treated with a solution of potassium cyanide, the cuprous cyanide dissolves as the double salt and the methyl iodide separates in oily drops.

When cuprous cyanide and methyl iodide are heated at 100° in the presence of excess of pure dry acetonitrile, the reaction proceeds

differently and a *compound*, CuNC,MeI, is formed almost quantitatively, which dissolves in the acetonitrile and crystallises from the latter in white needles. After traces of oily matter have been washed out with cold acetone, it can be purified by further crystallisations from acetonitrile. It is very sparingly soluble in all other ordinary organic solvents (Found for material dried at 100° : Cu, 28·0; I, 55·0. CuNC,MeI requires Cu, 27·45; I, 54·8%). When it is heated with a solution of potassium cyanide, methylcarbylamine is given off freely. The same double salt is obtained when cuprous cyanide and methyl iodide are heated to about 135°, but tarry products and cuprous iodide are also formed and the yield of CuNC,MeI is small.

Attempts to determine the molecular weight by the elevation of boiling point of acetonitrile gave very discordant results, but all pointed to a high value corresponding to about 3(CuNC,MeI). The stability of this substance as compared with the silver compounds is therefore probably due to the presence of a tricyanogen complex in the molecule.

On treatment with an aqueous solution of silver sulphate or nitrate, silver iodide, silver, and cupric salts are formed. A quantitative determination of the amount of silver iodide and silver produced showed that the action can be represented by the following equation (disregarding the complexity of the molecule) :

$$2CuNC,MeI + 2Ag_2SO_4 = 2AgI + 2Ag + CuSO_4 + Cu(NCMe)_2SO_4.$$

That the last compound is present in the solution, although it has not been isolated, seems probable since the liquid is at first almost odourless, but on evaporation in a vacuum over a dehydrating agent a strong smell of carbylamine develops. When the water has all been driven off, very little of the latter can be found in the crystalline residue, which consists almost entirely of copper sulphate, but still gives off a small quantity of carbylamine when warmed with potassium cyanide solution.

No means of isolating this cupric methylcarbylamine sulphate or the corresponding nitrate has been found.

In connexion with these experiments it was noticed that cuprous cyanide combines with acetonitrile with evolution of heat to form an unstable compound, CuNC,MeCN. The nitrile is gradually given off on exposure to the air. Other insoluble cyanides gave similar compounds, *e.g.*, silver ferrocyanide, silver ferricyanide, silver cobalticyanide, and nickelous cyanide. On the other hand, silver cyanide and zinc cyanide did not combine with the nitrile.

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