85. *Studies on Hydrogen Cyanide. Part XI. The Constitution of the Double Compound of Hydrogen Cyanide and Aluminium Chloride.*

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From a study of the action of bromine on hydrogen cyanide and its double compound with aluminium chloride ($AlCl_3,2HCN$) it has been shown that the latter compound is best represented as a molecular compound of aluminium chloride with iminoformylcarbylamine.

HYDROGEN cyanide reacts readily with aluminium chloride to yield the double compound $AlCl_3,2HCN$ (Hinkel and Dunn, J., 1931, 3243) and the dissociation of this compound (I) into its two components on dissolution in ether or on heating to 100° suggests that it is a simple molecular compound. On the other hand, the compound may be prepared from aluminium chloride and iminoformylcarbylamine (bimolecular hydrogen cyanide) (II), and on heating with hydrogen chloride it yields a compound (III) identical with that prepared directly from aluminium chloride and chloromethyleneformamidine (IV).

$$\begin{tikzcd}
AlCl_3 + 2HCN \arrow[r, shift left] & \underset{\text{(I.)}}{AlCl_3,2HCN} \arrow[l, shift left] \arrow[r, "HCl"] & \underset{\text{(III.)}}{AlCl_3,NH{:}CH{\cdot}N{:}CHCl} \arrow[d, shift left] \\
\underset{\text{(II.)}}{AlCl_3 + NH{:}CH{\cdot}NC} \arrow[ur] & & \underset{\text{(IV.)}}{AlCl_3 + NH{:}CH{\cdot}N{:}CHCl} \arrow[u, shift left]
\end{tikzcd}$$

The double compound (III) must therefore be formulated as shown, and compound (I) should then be $AlCl_3$,NH:CH·NC. The decomposition of this to yield hydrogen cyanide is surprising, however, since iminoformylcarbylamine can be passed through a strongly heated glass tube without undergoing decomposition or dissociation into hydrogen cyanide.

In order to test these views and to gain a further insight into the manner in which the hydrogen cyanide molecules are held in combination with the aluminium chloride, the action of bromine upon the double compound (I) has been investigated and compared with the action of bromine upon free hydrogen cyanide.

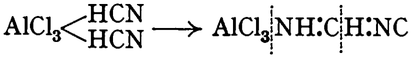
Bromine dissolves readily in anhydrous hydrogen cyanide to yield a red solution, and a vigorous reaction soon ensues with a brisk evolution of hydrogen bromide and rise of temperature, whilst a yellow to orange-red solid is formed, the colour probably being due to the presence of some perbromo-derivatives. The reaction is more readily followed in benzene solution, since, with the exception of cyanogen bromide and hydrogen bromide, all the products of the reaction between hydrogen cyanide and bromine are insoluble in benzene. The presence of cyanogen bromide in the benzene solution is recognised by its characteristic biting odour and by its conversion into cyaphenin and a mixture of bromobenzene and benzonitrile under the influence of aluminium chloride. From the coloured insoluble product, after treatment with benzene in presence of aluminium chloride, the following compounds were obtained: benzhydrylamine, benzaldehyde, and bromobenzene. The first two can only have been derived from the sesquibromide of hydrogen cyanide and bromomethyleneformamidine respectively (compare Gattermann and Schnitzspahn, *Ber.*, 1898, **31**, 1770; Hinkel and Dunn, J., 1930, 1834), whereas the last probably results from the red perbromo-compounds. There are, therefore, several reactions occurring almost simultaneously. The primary reaction must be the formation of cyanogen bromide ($HCN + Br_2 = CNBr + HBr$), the hydrogen bromide simultaneously produced combining almost immediately with more hydrogen cyanide to yield the sesquibromide as a white solid (compare Hinkel and Dunn, *loc. cit.*). With excess of hydrogen cyanide and under the influence of the heat of the reaction, some of the sesquibromide would be converted into bromomethyleneformamidine, according to the equations

$$2HCN,3HBr + 4HCN = 3(HCN)_2HBr$$
$$2HCN,3HBr - 2HBr = (HCN)_2HBr$$

When bromine is added to the compound $AlCl_3,2HCN$ in benzene suspension, at room temperature, a slow combination occurs which becomes more vigorous with increase of temperature. If this mixture is then heated without the further addition of aluminium chloride, a reaction occurs yielding as final product triphenylmethane. No reasonable explanation for this result can be formulated. If, however, the mixture is heated with an additional molecular proportion of aluminium chloride the usual Friedel–Crafts reaction sets in and the final product consists of benzophenone. In neither of these two reactions was any cyanogen bromide found, which would result if the hydrogen cyanide were loosely united as such with the aluminium chloride.

The formation of benzophenone follows naturally if the two molecules of hydrogen cyanide are united to the aluminium chloride as iminoformylcarbylamine. The bromine unites with the carbylamine group in a manner similar to that of hydrogen chloride, yielding the compound $AlCl_3,NH{:}CH{\cdot}N{:}CBr_2$, which in presence of free aluminium chloride and benzene would give rise to $AlCl_3,NH{:}CH{\cdot}N{:}CPh_2$, from which benzophenone results on hydrolysis.

From these reactions it would appear that the two molecules of hydrogen cyanide must be held united to the aluminium chloride as an unstable form of iminoformylcarbylamine, and that the aluminium chloride apparently weakens the bonds in the compound as indicated by dotted lines in (V) to facilitate the formation of hydrogen cyanide. On the other hand,



$$AlCl_3{<}{\begin{matrix}HCN\\HCN\end{matrix}} \longrightarrow AlCl_3\vdots NH{:}C\vdots H{:}NC$$

(V.)

the addition of hydrogen chloride to the carbylamine group must counteract this loosening effect, since, as already mentioned, the resulting compound (III) dissociates on heating into chloromethyleneformamidine and aluminium chloride.

EXPERIMENTAL.

Action of Bromine on Hydrogen Cyanide.—Bromine (28 c.c.; 1·25 mols.) was added to an ice-cooled solution of anhydrous hydrogen cyanide (32 c.c.; 2 mols.) in benzene (80 c.c.). The deep red solution soon became cloudy and a vigorous reaction ensued with a copious evolution of hydrogen bromide, and a pasty orange-red solid (A) separated. The mixture was kept overnight. To the decanted benzene solution, which had the characteristic biting odour of cyanogen bromide, powdered aluminium chloride (50 g.) was slowly added, the temperature of the mixture being gradually raised to 50° and maintained thereat for 5 hours. Hydrogen bromide was slowly evolved. The mixture was then poured on ice and hydrochloric acid, and the liquid filtered from the small quantity of dark brown solid, which, after being washed with cold alcohol, crystallised from glacial acetic acid in small branched crystals, m. p. 231°, not lowered by authentic cyaphenin, m. p. 232°. The combined benzene and water filtrate was distilled in steam, and the benzene distillate, after drying over calcium chloride, was distilled into fractions, b. p. 150—160° and b. p. 185—190°, consisting of bromobenzene (b. p. 157°) and benzonitrile (b. p. 191°) respectively.

Residue (A). To the flask containing the red solid were added benzene (100 c.c.) and then aluminium chloride (50 g.). As soon as the first rapid evolution of hydrogen bromide had ceased, the mixture was heated to 60° and the heating continued for 4 hours until there was no further evolution of hydrogen bromide. The mixture was poured on ice and concentrated hydrochloric acid, and the benzene and the water layer were decanted from the black viscous liquid (B) and treated as described in the previous experiment. The dried benzene solution so obtained yielded on distillation a small quantity of bromobenzene and a small residue, b. p. >180°, which contained nitrogen (probably due to benzonitrile) and also yielded a dinitrophenylhydrazone, m. p. 238°, unchanged when admixed with the dinitrophenylhydrazone of benzaldehyde.

Residue (B). The dark residue was hydrolysed by boiling with aqueous sodium hydroxide, and the dark red oil so obtained was dissolved in hot concentrated hydrochloric acid. On cooling, small needle-shaped crystals separated, m. p. 274°, unchanged by authentic benzhydrylamine hydrochloride.

Action of Bromine on $AlCl_3,2HCN$.—Hydrogen cyanide (8 c.c.; 2 mols.) was added to a suspension of finely powdered aluminium chloride (13·4 g.; 1 mol.) in benzene (80 c.c.) at 10°. The mixture was gently stirred for 30 mins. in order to ensure the complete formation of the double compound $AlCl_3,2HCN$. Bromine (5·5 c.c.; 1 mol.) was then added. Gradual union with the aluminium compound occurred, yielding a dark-coloured heavy liquid immiscible with the benzene (product C). To the well-stirred mixture, powdered aluminium chloride (13·4 g.; 1 mol.) was added, and the temperature of the mixture gradually raised to 75°, whereupon a rapid evolution of hydrogen bromide occurred. The heating and stirring were continued until evolution of hydrogen bromide ceased (4 hrs.). The reaction mixture was then poured on ice and concentrated hydrochloric acid, and the benzene removed by steam. Further steam-distillation yielded an aqueous distillate containing a yellow oil. Extraction with ether and subsequent removal of the ether yielded a yellow oil which, without further purification, was converted into a phenylhydrazone, m. p. 137°, unchanged by authentic benzophenonephenylhydrazone.

If the benzene mixture (product C) was heated without the further addition of aluminium chloride and subjected to the subsequent treatment as previously described, the aqueous distillate obtained after removal of benzene yielded oily drops which solidified on cooling and were identified as triphenylmethane, m. p. 93°, unchanged by an authentic specimen. No benzophenone was obtained under these conditions.

The authors' thanks are due to the Chemical Society for a grant, and to Imperial Chemical Industries, Ltd., for a grant and gifts of chemicals.

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[*Received, February* 14*th*, 1940.]