Hydrogen Cyanide as a Ligand in Liquid Hydrogen Fluoride

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SILVER CYANIDE, a linear polymer in the solid state, is soluble to the extent of about 3·2M in anhydrous hydrogen fluoride (HF) at 20°; these solutions conduct with $\Lambda_0 = 358 \pm 5$ cm.^{2} ohm^{-1} M^{-1} at 0°, this value being similar to that (391) measured for both NaF and KF solutions in HF at this temperature.[1] The proton magnetic resonance (^{1}H n.m.r.) spectrum of AgCN in HF at 60 Mc./sec. shows only one solute resonance (width at half-height 2·0 c./sec.) 99·9 c./sec. downfield from internal tetramethylammonium ion (TMA).[2] The resonance was shown to be equivalent to one proton per AgCN by using TMA as a quantitative internal proton standard. The ^{13}C satellites were observed for solutions containing ^{13}C-enriched AgCN and the value for $J(^{13}$C–H) of 291 c./sec. is taken to indicate that the proton is bonded to carbon rather than to nitrogen. The size of the coupling constant indicates that the carbon atom is *sp*-hybridised.[3] Hydrogen cyanide is essentially a non-electrolyte in solution in HF, and its ^{1}H n.m.r. spectrum exhibits one solute resonance (width at half-height 2·5 c./sec.) 77·2 c./sec. downfield from TMA with $J(^{13}$C–H) = 282·5 c./sec. Hydrogen fluoride solutions of mixtures containing different HCN : Ag$^+$ molar ratios (from 4 : 1 to 1 : 7·5) show only one proton resonance at 32°; the observed chemical shifts are shown in the Figure as a function of the molar proportions of HCN : Ag$^+$.

The infrared spectrum of AgCN in HF in the region 2000 to 2200 cm.$^{-1}$ shows an absorption at 2147 cm.$^{-1}$ (E^{t}_{max} 153, calculated[4] on the basis of the silver concentration) with a shoulder at 2138 cm.$^{-1}$. The relative intensities of these bands may be altered by varying the HCN : Ag^+ ratio in the solution. Thus the band at 2147 cm.$^{-1}$ is strongest (E^{t}_{max} 378) at a ratio HCN : $Ag^+ = 2 : 1$, and at this composition the band is symmetrical. However, at ratios exceeding 2 : 1 a shoulder again appears at 2138 cm.$^{-1}$.

We propose that AgCN dissolves in HF according to the following reaction scheme.

$$2AgCN + 2HF \rightarrow$$

$$2HCNAg^+ + 2F^- \rightleftarrows (HCN)_2Ag^+ + Ag^+ + 2F^-$$

This is consistent with AgCN behaving as a 1 : 1-electrolyte. The infrared absorption at 2147 cm.$^{-1}$ is attributed to the ion $(HCN)_2Ag^+$ and the absorption at 2138 cm.$^{-1}$, when the ratio HCN : $Ag^+ < 2 : 1$, to the ion $HCNAg^+$. A solution of HCN in HF also absorbs at 2138 cm.$^{-1}$, but it decomposes with a half-life of 45 hours as shown by a decrease in the intensity of the infrared absorption. However, a solution of AgCN in HF showed no change in the infrared spectrum for 100 hours; we therefore consider that no uncomplexed HCN is present in such a solution. The absorption at 2138 cm.$^{-1}$ of solutions in which the ratio HCN : $Ag^+ < 2 : 1$ is not due to HCN but to the ion $HCNAg^+$. Addition of HCN to a solution of AgCN results in no increase in the absorption at 2138 cm.$^{-1}$, rather in an increase in the absorption at 2147 cm.$^{-1}$ due to the reaction $HCNAg^+ + HCN \rightarrow (HCN)_2Ag^+$. Reduction of the HCN : Ag^+ ratio to less than one, however increases the absorption at 2138 cm.$^{-1}$ due to the equilibrium $(HCN)_2Ag^+ + Ag^+ \rightleftarrows 2HCNAg^+$, and at a ratio HCN : $Ag^+ = 1 : 4$ the two bands can be resolved. Relating the extinction coefficients of the 2147 cm^{-1} absorptions of a solution of AgCN and of a solution containing HCN : Ag^+ in the ratio 2 : 1, we calculate that the solution of AgCN contains 40·5% of the silver present as the ion $(HCN)_2Ag^+$ and, therefore, 19% as the ion $HCNAg^+$.

The ^{1}H n.m.r. results shown in the Figure are fully consistent with the above hypothesis. Solutions containing one or more of the species $HCNAg^+$, $(HCN)_2Ag^+$, and HCN show only one resonance due to rapid exchange of HCN; the position of resonance, therefore, depends only on the relative concentrations of the species present. The ^{13}C satellites were observed from solutions in HF of AgCN and HCN enriched with ^{13}C, and, therefore, rapid exchange of the proton with solvent protons does not occur. We assume that when the ratio HCN : $Ag^+ = 2 : 1$ all the HCN is complexed as the ion $(HCN)_2Ag^+$, the position of resonance of this ion being 102·4 c./sec. downfield from TMA. We have no evidence for an ion of co-ordination number higher than two, either from ^{1}H n.m.r. or from infrared data. Extrapolation of the ^{1}H n.m.r. data back to a zero HCN : Ag^+ ratio gives the position of resonance of the ion $HCNAg^+$ to be 92·2 c./sec. downfield from TMA. From these values we calculate that when AgCN is dissolved in HF the cations present are $(HCN)_2Ag^+$ and Ag^+, 37·7% each, and $HCNAg^+$, 24·5%. These results are in satisfactory agreement with the values obtained from the infrared data. The ^{1}H n.m.r. results also indicate that the absorption in the infrared at 2138 cm.$^{-1}$ when the ratio HCN : $Ag^+ > 2 : 1$ is due to HCN.

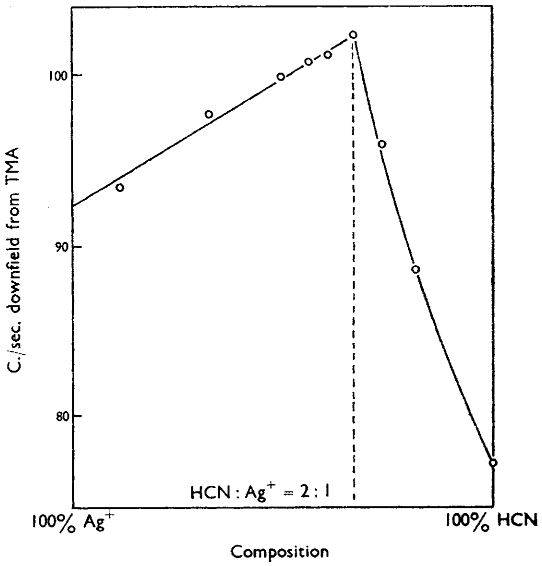

FIGURE. *Influence of the* HCN : Ag^+ *molar composition on the observed chemical shift.*

(*Received, May* 1*st,* 1967, *Com.* 422.)

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