PREPARATION OF DRY HYDROGEN CYANIDE, ETC. 255

XXIII.—Preparation of Dry Hydrogen Cyanide and Carbon Monoxide.

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It is obvious that, by the action of sulphuric acid on potassium cyanide, both hydrogen cyanide and carbon monoxide may be formed, but it does not seem to be generally known that by suitably varying the concentration of the acid, a practically quantitative yield of either product can be obtained.

The alkali cyanide is of course decomposed by sulphuric acid of all concentrations, and on distillation with the dilute acid yields dilute hydrocyanic acid; with a less dilute acid, however, less water passes over, and with a mixture of equal volumes of sulphuric acid and water, the hydrogen cyanide contains only such small quantities of aqueous vapour as are readily removed by passing it over warm calcium chloride.

When a larger proportion of sulphuric acid is used, a certain amount of carbon monoxide is formed, and as the concentration of the acid is increased the volume of gas increases, whilst the amount of hydrogen cyanide diminishes; and finally, when ordinary concentrated sulphuric acid is allowed to act on the cyanide, nearly pure carbon monoxide is evolved in almost theoretical quantity.

Preparation of Dry Hydrogen Cyanide.

In preparing hydrogen cyanide free from water, ordinary 98 per cent. lump cyanide (100 grams), in pieces of the size of a hazel nut, is placed in a capacious flask, provided with a drop-funnel and delivery tube, the latter being connected through two U-tubes of calcium chloride with a series of two Y-tubes (U-tubes furnished with tubuluses), the stems of which pass through the necks of inverted bell-jars into two receiving bottles. The drying tubes are immersed in a vessel of water at about 35°, and are filled respectively with pieces of fused calcium chloride and fragments of the well-dried porous material. The condensing tubes are cooled, the first with ice and water, and enough salt to reduce the temperature to about -10° , the second with ice and salt at about -20° ; it is not advisable to cool the first tube much below the temperature specified, or the tubulus may become choked with crystals of the frozen acid. The receiving bottles are cooled with ice, and closed with corks through which the tubuluses pass. The great bulk of the acid collects in the first receiver, only 2 or 3 per cent. passing on to the second, and practically none escapes condensation.

A current of air having been blown through the drying and condensing tubes, to dry the latter, and the cooling and warming baths brought to the requisite temperatures, a cold mixture of equal volumes of sulphuric acid and water (100 c.c. of each) is allowed to drop on to the cyanide at such a rate that about one drop of hydrogen cyanide falls into the first receiver per second. As each drop of acid reaches the cyanide, there is a brisk effervescence and frothing, with development of heat, the mixture becoming sufficiently hot to retain the potassium hydrogen sulphate in solution. At the end of the action, the vapour in the flask and solution is expelled by heating the latter to incipient ebullition.

In this way, with the quantities specified, about 40 grams (58 c.c.) of practically pure hydrogen cyanide is obtained, which on rectification from a little phosphorus pentoxide over a bath of warm water, passes over entirely between $26 \cdot 2^{\circ}$ and $26 \cdot 3^{\circ}$. The average yield of the pure

substance is 38.5 grams, the calculated amount being 40.8 grams; the maximum yield obtainable from 100 grams of potassium ferrocyanide is 15.3 grams.

Preparation of Carbon Monoxide.

In preparing carbon monoxide from potassium cyanide, the same generating apparatus is used, cold concentrated sulphuric acid being substituted for the diluted acid. The gas is purified from accompanying hydrogen cyanide vapour, and in certain eventualities from carbon and sulphur dioxides, by washing twice with strong potash solution; as a rule, it is quite free from carbon dioxide, but commercial lump cyanide sometimes contains a little carbonate.

If the acid is allowed to flow too fast on to the cyanide, so that the temperature becomes unduly high, the sulphuric acid is reduced, and sulphur and carbon dioxides are formed; but this does not occur if the action is kept within moderate bounds. Even with a slow delivery of the acid, the evolution of the gas is very rapid, and several litres may be prepared in a few minutes.

The yield of pure carbon monoxide, completely soluble in cuprous chloride solution, obtained in this way from 50 grams of cyanide, varies from 14 to 16 litres, the calculated quantity at 15° and 760 mm. being 17.4 litres, moreover, the process is quite as convenient as the formic acid process, and much more economical.

The action of concentrated sulphuric acid on anhydrous hydrogen cyanide is similar. The mixture soon becomes hot, but although some of the cyanide is of course volatilised, the greater part enters into combination, and on applying heat abundance of carbon monoxide is evolved. If the liquid is overheated, or even in the cold, if sufficient time is allowed, carbon and sulphur dioxides are formed, as with the alkali cyanide.

The Mechanism of the Carbon Monoxide Reaction.

It would appear at first sight that the quantitative conversion of the carbon of potassium cyanide into carbon monoxide is effected by ordinary hydrolysis and dehydration, the hydrogen cyanide being converted into formic acid, and this into carbon monoxide. Whether hydrogen cyanide be formonitrile, $H \cdot C$:N, or what may be termed carbamine, $H \cdot N$:C, the same products of hydrolysis will be formed : from the nitrile a carboxylic acid (formic acid) and ammonia, and from the carbamine, an amine (ammonia) and formic acid. Sufficient water for the purpose is indeed present in ordinary concentrated sulphuric acid, assuming the complete action to be represented by some such equation as

$$\label{eq:KCN} \begin{split} & \mathrm{KCN} + 2\mathrm{H}_2\mathrm{SO}_4 + \mathrm{H}_2\mathrm{O} = \mathrm{KHSO}_4 + \mathrm{NH}_4 \cdot \mathrm{HSO}_4 + \mathrm{CO}. \\ & \text{vol. LXXIII.} & \mathrm{S} \end{split}$$

RICE: MANGANIC SALTS.

But the change is equally well brought about by a mixture of two volumes of concentrated sulphuric acid with one of Nordhausen acid, in which water can hardly be present, and it is therefore probable that part, at all events, of the latter is derived from the acid sulphate. This point would scarcely be worth attention, were it not that potassium hydrogen sulphate itself behaves in a closely parallel manner.

On heating an intimate mixture of the dry salt with dry potassium cyanide in an air bath at $230-250^{\circ}$, anhydrous hydrogen cyanide distils over, and may be collected in the apparatus described above, the yield corresponding with about 55 per cent. of the total cyanogen; this, of course, is the action which would naturally be expected,

 $KCN + KHSO_4 = K_2SO_4 + HCN.$

But a large amount of carbon monoxide is also evolved at all stages of the action, and the residue left in the flask after the action has ceased smells strongly of ammonia, and dissolves in water, forming a strongly alkaline solution. As this carbon monoxide and ammonia are formed by the interaction of anhydrous substances, the hydrolytic water is necessarily derived from the potassium hydrogen sulphate, in accordance with such equations as the following :

$$\begin{split} & \text{KCN} + 3\text{KHSO}_4 = \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{CO} + \text{NH}_3 \text{ ;} \\ & 2\text{KCN} + 8\text{KHSO}_4 = 3\text{K}_2\text{SO}_4 + 2\text{K}_2\text{S}_2\text{O}_7 + 2\text{CO} + (\text{NH}_4)_2\text{SO}_4. \end{split}$$

It would thus appear that both sulphuric acid and potassium hydrogen sulphate can behave at the same instant and under the same conditions both as hydrolytic, and as dehydrating agents.

Anhydrous potassium ferrocyanide, it may be mentioned, interacts with potassium hydrogen sulphate in a similar manner, about 40 per cent. of the cyanogen being converted into hydrogen cyanide, and about 10 per cent. into carbon monoxide and ammonia, the residual 50 per cent. remaining in combination as potassium ferrous ferrocyanide, as in the ordinary method of preparing dilute hydrocyanic acid. With excess of acid sulphate and at a high temperature, carbon and sulphur dioxides are evolved in abundance, as with the simple cyanides.

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