CXVIII.—*Hydroferrocyanic Acid.*

By KENDALL COLIN BROWNING, B.A.

AMONG the many apparently contradictory statements made concerning the properties of hydroferrocyanic acid, are those referring to the action of heat on the substance.

Robiquet (*Ann. Chim. Phys.*, 1819, [i], **12**, 277) obtained anhydrous hydrocyanic acid by heating hydroferrocyanic acid to the boiling point of mercury. On further raising the temperature, nitrogen was evolved, and a black powder left, which, with caustic potash, gave a trace of potassium ferrocyanide, and on boiling evolved traces of ammonia. The residue was non-magnetic, contained carbon, and was regarded as a mixture of iron and carbon.

Berzelius (*Ann. Chim. Phys.*, 1820, [i], **15**, 228) heated ammonium ferrocyanide and obtained iron cyanide. This substance, at a low red heat, evolved nitrogen and left iron carbide. No analyses are given in the paper.

Rammelsberg (*Pogg. Ann.*, 1851, **38**, 364; **42**, 111) states that by heating hydroferrocyanic acid he obtained ferrous cyanide, and at a "higher temperature" paracyanogen and a substance $C_{10}N_5Fe_6$.

Etard and Bémont (*Compt. rend.*, 1884, **99**, 972, 1024) say that dry hydroferrocyanic acid at 440° evolves 46 per cent. of hydrocyanic acid, leaving a yellow mass, $FeHFeCy_5$ or $2FeCy_2,HCy$.

The acid used in the following work was obtained by adding pure hydrochloric acid to a cold saturated solution of purified potassium ferrocyanide. It was dissolved in absolute alcohol, precipitated by dry ether, dried at 80—90° in hydrogen and then in a vacuum, and redissolved in absolute alcohol. This process was repeated five times, until potassium could no longer be detected spectroscopically.

The following results were obtained on analysis:

Found, Fe = 25·85, 25·80, 25·998. Calc., Fe = 26·04 per cent.

Thus obtained, the acid is a snow-white mass. It obstinately retains ether, and this is best removed by heating to 80° for some hours in a current of hydrogen dried by phosphoric oxide, and finally raising the temperature to 100°.

Decomposition of Hydroferrocyanic Acid in Air.

When dry and free from ether, hydroferrocyanic acid remains unchanged when exposed to air, over phosphoric oxide, for many months.

On gentle warming in air, it turns blue, evolving hydrocyanic acid, and when heated for a few days to just over 100°, it completely oxidises to ferric oxide. As would be expected, it deflagrates when mixed with sodium peroxide and gently warmed. When warmed to 60° with water free from air, it evolves hydrocyanic acid, leaving ferrous cyanide (compare Adie and Browning, Trans., 1900, **77**, 150).

Action on Ether.

When dry hydroferrocyanic acid is treated with absolute ether, a considerable evolution of heat occurs, and the mass swells up. According to Etard and Bémont (*loc. cit.*), the compound $H_4FeCy_6,2Et_2O$ is obtained, but they give no analyses or details.

Dry hydroferrocyanic acid was therefore exposed to absolute ether vapour for a few weeks, and then kept in a desiccator over paraffin till the weight was approximately constant. Analyses gave:

Ether = 28·06 and 28·29 per cent.

$H_4FeCy_6,2Et_2O$ requires ether = 40·66 per cent.
H_4FeCy_6,Et_2O „ ether = 25·5 „

By very gently warming in dry air for some days, almost every trace of ether was expelled, so no very definite compound seems to exist under these conditions.

Action of Heat in absence of Oxygen.

The decomposition described below was effected in hard glass vessels which were heated in a bath of Wood's metal. Owing to the ease with which the products oxidise, the whole apparatus was repeatedly exhausted by a mercury pump, and filled with purified hydrogen dried by phosphoric oxide.

A manometer was used to show when gas evolution commenced, and afterwards a very slow current of hydrogen was passed to sweep out the last traces of hydrocyanic acid. Temperatures were taken by a mercury thermometer filled with nitrogen under pressure.

A very slow evolution of hydrocyanic acid begins at 120°, but even when heated at 220° for 3 hours the decomposition is not complete, the product containing undecomposed hydroferrocyanic acid.

Found, Fe = 44·2 and 44·3 per cent.

$FeCy_2$ requires Fe = 51·8 per cent.
$FeCy_2{\cdot}HCy$,, Fe = 41·4 ,,
$2FeCy_2{\cdot}HCy$,, Fe = 46·1 ,,

At 300°, however, the decomposition was rapid, and was complete in less than two hours. The whole of the hydrocyanic acid was evolved and a pale yellow powder, which analysis showed to be ferrous cyanide, was left.

Found, Fe = 51·4, 51·2. $FeCy_2$ requires Fe = 51·8 per cent.

The difference is undoubtedly due to the ease with which ferrous cyanide undergoes oxidation. Even in cold air it rapidly becomes warm, turning greenish-yellow, slate-blue, and finally deep blue, and when warmed gently, it glows, burning to ferric oxide.

This decomposition of hydroferrocyanic acid gives a convenient and moderately safe method of preparing dry, colourless hydrocyanic acid.

Ferrous cyanide is stable, in absence of oxygen, up to 430°, but above that temperature it very slowly evolves nitrogen. The evolution becomes more rapid on raising the temperature, but is not complete even after six hours heating at about 480°. For example, a specimen gave Fe = 67·3, FeC_2 requiring Fe = 70 per cent.

By heating to dull redness in a lead-bath for 4 hours, all the nitrogen was evolved and a black mass left, which had a composition approximating to that required for the carbide FeC_2.

Found, Fe = 70·4, 70·7, 70·5. FeC_2 requires Fe = 70·0 per cent.

The excess of iron seems due to slight reduction of the cyanide by the small amount of hydrogen present in the vessel.

The black mass left is a very fine powder, and when gently warmed it glows, oxidising to ferric oxide, hence great care must be taken to remove all oxygen from the apparatus in which the ferrous cyanide is prepared. It partially dissolves in dilute hydrochloric or sulphuric acids, evolving hydrogen and small quantities of hydrocarbons. With nitric acid of sp. gr. 1·35, it partially dissolves, giving the usual coffee-coloured solution, indicating the presence of a carbide. The substance, however, is not pure iron carbide, FeC_2, as

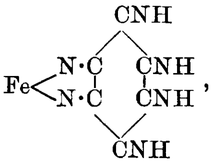
(i) It partially and readily dissolves in dilute hydrochloric acid, and the residue dried in a vacuum at 160°, or over phosphoric oxide in a vacuum for three weeks, only contains about 29 per cent. of iron (found, Fe = 29·0, 29·3 per cent.).

(ii) The residue left after repeated treatment with acid is pure carbon only. The carbide present is not due to reaction between the iron and carbon formed by decomposition of the cyanide, as by heating an intimate mixture of reduced iron and carbon powder for 3 hours at the temperature of complete decomposition of ferrous cyanide, no trace of carbide could be detected by the nitric acid reaction.

Hence it would seem that ferrous cyanide decomposes chiefly to iron, carbon, and iron carbide. The product contains no cyanide, but by treating with hydrochloric acid and then with caustic potash, a trace of ammonia was evolved, so apparently a trace of iron nitride is formed (compare Fowler, *B.A. Report*, 1893; Abstr., 1894, ii, 50).

Constitution of Ferrous Cyanide.

According to Friedel's suggestion (note to a paper by Muller, *Compt. rend.*, 1887, **104**, 994), hydroferrocyanic acid is



and, unless tautomeric change occurs in the decomposition, ferrous cyanide should be an *iso*cyanide.

Although ferrous cyanide does not react with ethyl iodide even when heated with it and alcohol for many hours, yet when warmed in a current of hydrogen with potassium ethyl sulphate, ethyl *iso*cyanide was obtained and was readily identified. This reaction would tend to confirm the *iso*cyanide formula, as ethyl cyanide is not transformed to the *iso*cyanide at the temperature used (200—220°).

Lastly, Wade (Proc., 1900, **16**, 156) has shown that the effect of heat is to transform a metallic *iso*cyanide into the normal form, and not *vice versâ*, just as is the case with many organic *iso*cyanides. Wade finds that potassium cyanide is really an *iso*cyanide, and undergoes transformation into the normal form on heating strongly; ferrous cyanide also behaves in a similar manner.

If ferrous cyanide were $Fe(CN)_2$, then it would be expected to leave iron carbide when all nitrogen is expelled, whereas if it has the isomeric structure $Fe(NC)_2$, it should give iron, carbon, and possibly a trace of nitride. As a matter of fact, the product is a mixture of iron, carbon, iron carbide, and possibly a trace of nitride, so it would seem that the ferrous cyanide group has the latter constitution in hydroferrocyanic acid, but when decomposing at about 500° behaves as if it were a mixture of the cyanide and *iso*cyanide.

Constitution of Hydroferrocyanic Acid.

Owing to the ease with which a hydrogen atom shifts from one position to the other, it is almost impossible to decide from the behaviour of free hydrocyanic acid whether in hydroferrocyanic acid the four HCN groupings have the *iso*- or normal arrangement. Brühl (*Ber.*, 1883, **26**, 806) states that, from its molecular refraction, hydrocyanic acid would seem to have a constitution different from that of cyanogen, which he has shown has a molecular refraction agreeing with that calculated for the constitution $N{:}C\cdot C{:}N$; it must therefore be $HN{:}C$ or $HN{\vdots}C$. In a later paper, however (*Zeit. physikal. Chem.*, 1895, **16**, 497), he concludes that the acid is $HC{:}N$, as its molecular refraction (for sodium light) agrees with that of the aliphatic cyanides.

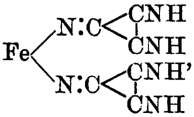
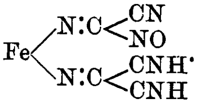
The *iso*cyanide formula is, however, supported by Nef's work on bivalent carbon (*Annalen*, 1892, **270**, 267; 1895, **287**, 265; compare also Thiele, *Ber.*, 1883, **26**, 2645). For example, hydrocyanic acid readily combines with ethyl hypochlorite to form ethyl cyanimidocarbonate, $C{:}N\cdot C(NH)\cdot OC_2H_5$. Further, in presence of alcohol, it first forms (with hydrogen chloride) imidoformyl chloride, $NH{:}CHCl$, and then the compound $NH{:}CH\cdot C(NH)Cl$.

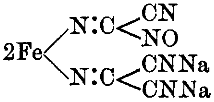
Kieseritzky (*Zeit. physikal. Chem.*, 1899, **28**, 385), from the results obtained by an electrometric method of determining constitution, concludes that hydrocyanic acid is $H\cdot NC$.

The above work, however, does not obviate the possibility of tautomerism, and indeed the fact that dry hydrocyanic acid is very inert and does not combine with chlorine or hydrogen chloride at low temperatures, or with ethyl hypochlorite at $-10°$, tends to show that under some conditions hydrocyanic acid behaves as if it were $H\cdot CN$.

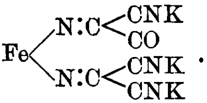
Hence it does not seem possible, from examination of the hydrocyanic acid prepared from hydroferrocyanic acid, to draw any very definite conclusion as to the constitution of the latter. The decomposition of ethyl ferrocyanide was therefore examined.

Ethyl ferrocyanide was first prepared by Freund (*Ber.*, 1888, **21**, 931) by washing precipitated silver ferrocyanide with strong alcohol, and heating it, without further drying, with alcohol and ethyl iodide; the yield, however, is unsatisfactory. A better method is to dry silver ferrocyanide over phosphoric oxide in a vacuum, grind it to an impalpable powder, mix with twice its weight of dry sea-sand, and heat under pressure with absolute alcohol and slight excess of ethyl iodide for 12 hours at 100° (the yield is not improved by heating at 130° in an autoclave). The mass is then repeatedly extracted with absolute alcohol, evaporated down, recrystallised from chloroform, and dried in warm air, or recrystallised from excess of boiling acetone.

According to Freund, the ester decomposes on heating, giving ethyl *iso*cyanide. His experiments were repeated, and confirmed in every detail. The free acid would therefore seem to be $4H\cdot NC(FeNC)_2$, agreeing thus with Friedel's formula. In support of this ring formula, the stability of most ferrocyanides when heated may be quoted, but no other satisfactory evidence has been adduced. It does not, however, easily explain (i) the ready formation of nitroprussides by the action of nitric acid on ferrocyanides, or of nitroprussic acid by the action of nitric oxide on a warm aqueous solution of hydroferrocyanic acid (Playfair, *Phil. Mag.*, 1850, [iii], **36**, 197, 271, 348), or by the action of potassium nitrite on ferricyanides at 100° (Prud'homme, *Compt. rend.*, 1890, **111**, 45); (ii) the transformation of nitroprussides into ferrosotetracyanides on heating (Etard and Bémont, *Compt. rend.*, 1885, **100**, 275), $2Na_2NOFeCy_5 = 2Na_2FeCy_4 + 2NO + C_2N_2$. If, however, we assume that hydroferrocyanic acid is , then nitroprussides become salts of the acid . Their decomposition, on heating, would be readily explained thus:

 $= 2NO + C_2N_2 + 2Na_2FeCy_4$,

and potassium carbonylferrocyanide (Muller, *loc. cit.*) would be

.

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