XVI.—*The Interaction of Sulphuric Acid and Potassium Ferrocyanide.*

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THE interaction of concentrated sulphuric acid and potassium ferrocyanide seems to have been first investigated by Döbereiner (*Schweigger's Journ.*, 1820, **28**, 107), who stated that pure carbon monoxide is formed (compare Berzelius, *ibid.*, 1820, **30**, 57).

Fownes (*Phil. Mag.*, 1844, [iii], **24**, 21), apparently in ignorance of Döbereiner's previous work, to which he does not allude, found that nearly pure carbon monoxide is formed, accompanied at first with traces of hydrocyanic acid and carbon dioxide. The residue consisted chiefly of ferrous, ammonium, and potassium hydrogen sulphates. Towards the end of the reaction, ferric sulphate and sulphur dioxide were formed, and crystals of anhydrous iron ammonium alum deposited.

Merk (*Repert. Pharm.*, 1839, **68**, 190), by rapidly distilling potassium ferrocyanide with sulphuric acid, obtained a distillate containing a little prussic acid, thiocyanic acid, and formic acid; he also obtained a sublimate of needle-shaped crystals of ammonium sulphite.

Everitt (*Phil. Mag.*, 1835, [iii], **6**, 97) first showed that, with dilute sulphuric acid in slight excess, hydrocyanic acid is given off and a new salt, Everitt's salt $K_2Fe_2(CN)_6$, left.

Wittstein (*Vierteljahr. Pharm.*, 1854, **4**, 515), Aschoff (*Arch. Pharm.*, 1860, [ii], **106**, 257), and Williamson (*Annalen*, 1846, **57**, 225, and *Memoirs Chem. Soc.*, 1848, **3**, 125) also investigated the reaction.

Considering the differences between the conclusions of these investigators and the almost complete absence of quantitative results, the authors have investigated the decomposition of potassium ferrocyanide by sulphuric acid of concentrations varying from that of the approximately pure acid containing 98 per cent. H_2SO_4, to that of the acid represented by $H_2SO_4,18H_2O$. The potassium ferrocyanide used was recrystallised until no impurity could be detected. It was dried at 104—105° until its weight was constant, and kept in a desiccator over phosphoric oxide. The sulphuric acid used was freshly distilled and was free from dissolved sulphur dioxide.

Estimation of Carbon Monoxide.

A weighed amount of ferrocyanide was introduced into a small flask or wide test-tube, which could be heated in an oil-bath, and the apparatus completely filled with dry carbon dioxide. The sulphuric acid was then run in by means of a tap-funnel and the vessel heated, a slow current of carbon dioxide being maintained. The carbon monoxide was collected over aqueous caustic potash (1 : 2). Temperatures were taken during the reaction by means of a thermometer immersed in the acid.

Estimation of Hydrocyanic Acid.

The anhydrous salt was placed in a flask and the apparatus filled with hydrogen, free from oxygen. The acid was run in and the mixture distilled into two sets of potash bulbs. In order to keep the concentration of the acid constant, a small double surface condenser was used, and at the end of each estimation its temperature was raised to 100° to expel all traces of hydrocyanic acid * from the apparatus. The solution was then washed out of the potash bulbs, diluted, and the hydrocyanic acid estimated by standard silver nitrate, using sodium chloride as indicator.

Action of 98 *per cent. Sulphuric Acid.*

When mixed with excess of 98 per cent. sulphuric acid, potassium ferrocyanide, dried as described, turned white and then dissolved. Although a *trace* of hydrocyanic acid was evolved at first, no carbon dioxide was given off and no measurable quantity of carbon monoxide was obtained, even after heating for two hours at 100°. When the temperature was raised to 130°, decomposition set in, but was slow even at 200°, at which temperature the acid fumed strongly, and sulphur dioxide was evolved.

Quantitative experiments showed that the reaction was very slow and incomplete. Carbon monoxide is only formed in any appreciable quantity at a temperature above 200°, and approximating to that of the formation of fumes. The action increased slowly on further raising the temperature, but even after $2\frac{1}{2}$ hours at 200—210° the yield of carbon monoxide amounted only to about 4 per cent. of the theoretical, being dependent on the temperature and time of heating.

The authors confirm Fownes' observation of the formation of crystals containing potassium and ammonium ferric sulphates towards the end of the reaction.

To ascertain the nature of the reaction taking place in the solution, dry potassium ferrocyanide was dissolved in 48 per cent. sulphuric acid at 100° in an atmosphere of carbon dioxide, the solution cooled in a freezing mixture, and ether added. The white precipitate obtained was collected by the aid of a Pasteur filter in an atmosphere of hydrogen, dried, dissolved in absolute alcohol, and reprecipitated by ether. This process was repeated three times, and the white, crystalline product dried in a vacuum over phosphoric oxide. Its properties and determinations of the iron by means of mercuric oxide, and by sulphuric acid showed it to be hydroferrocyanic acid.

Action of H_2SO_4,H_2O.

The reaction was carried out on similar lines to the foregoing, and, although more rapid, was still slow; gas bubbles appeared at about 170°, simultaneously with slight fuming. The action became more rapid at 195—200°, but was not complete at the end of an hour, even with a large excess of the acid. Thus 0·2832 gram of anhydrous

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* Blank experiments showed that hydrocyanic acid was completely expelled from the condenser by this means.

potassium ferrocyanide gave 85·8 c.c. (corr.) of carbon monoxide in 1 hour, the calculated volume being 103·4 c.c.

Action of $H_2SO_4,2H_2O$.

The reaction was steady, the salt dissolved completely, and carbon monoxide began to be slowly evolved at about 130°. At 175—180°, the evolution was rapid, and the reaction was complete in about 35—40 minutes. The yield of carbon monoxide accounted quantitatively for the amount of carbon in the ferrocyanide, and no measurable quantity of hydrocyanic acid could be detected.

	CO at 0° and 760 mm. Found.	Calc.
0·1388 gram $K_4Fe(CN)_6,3H_2O$ gave......	44·6 c.c.	44·2 c.c.
0·2125 „ $K_4Fe(CN)_6,3H_2O$ „	77·6 „	78·0 „

Action of $H_2SO_4,4H_2O$.

With increased dilution, the reaction began to change, hydrocyanic acid being formed in quantity, as well as carbon monoxide, and a small quantity of a solid substance was precipitated. A small quantity of formic acid was also detected, both in the absorption bulbs and in the flask. The carbon monoxide was given off below 120°, but the hydrocyanic acid only came off slowly, even with brisk boiling, at this temperature, as shown by the following three experiments:

Time.	HCN [calc. as 6HCN per mol. $K_4Fe(CN)_6$].
1¼ hours	2·6 per cent.
3¼ „	6·02 „
7 „	8·80 „

Taking the highest of these numbers, we obtain

Mass $K_4Fe(CN)_6$.	Vol. CO at 0° and 760 mm. (found).	HCN per cent. (found).	CN per cent. (calc.).
0·2241 gram.	6·99 c.c.	—	3·7
0·8964 „	—	8·83	8·43

The sum of these two amounts of cyanogen does not account for the whole of this radicle, the theoretical percentage being 36·96, so that the amount of formic acid obtained had to be estimated.

As it is difficult to estimate formic acid in presence of Everitt's salt, &c., by ordinary methods, it was determined from the amount of ammonia formed in the hydrolysis of the cyanide groups, as in the Kjeldahl method. The total ammonia obtained represents carbon monoxide as well as formic acid, hence the amount of the latter is obtained by subtracting the ammonia corresponding to the carbon monoxide from the total and calculating the difference as formic acid.

The amount of formic acid which was at a maximum with this strength of acid* was represented only in milligrams, and consequently was too small to affect the result.

The solid residue consisted of Everitt's salt, which is only slowly decomposed, mixed with a certain amount of ferrous and other sulphates in solution. Hence, in this case, the main products of the reaction are carbon monoxide and hydrocyanic acid, mixed in about the ratio 3·7 : 8·43.

Action of $H_2SO_4,6H_2O$.

With acids of less concentration than $H_2SO_4,4H_2O$, for example $H_2SO_4,6H_2O$, the reaction showed a marked change in character,

Acid.	$K_4Fe(CN)_6$.	HCN [calc. as 6HCN per mol. $K_4Fe(CN)_6$].	Time.
$H_2SO_4,4H_2O$ (Everitt's salt left)	0·7326 grams.	2·7 per cent.	1¼ hours.
	0·6997 ,,	6·3 ,,	3¼ ,,
	0·8964 ,,	8·8 ,,	7 ,,
$H_2SO_4,6H_2O$ (Everitt's salt left)	0·9722 ,,	10·3 ,,	1¼ ,,
	0·9432 ,,	16·8 ,,	3¼ ,,
	0·8088 ,,	39 ,,	6½ ,,
$H_2SO_4,8H_2O$ (Everitt's salt left)	2·2074 ,,	24·5 ,,	2 ,,
	0·8463 ,,	36·6 ,,	2 ,,
	1·1114 ,,	47 ,,	3 ,,
	0·8536 ,,	71 ,,	6 ,,
$H_2SO_4,10H_2O$ (No Everitt's salt left)	1·3180 ,,	30 ,,	1 ,,
	1·1356 ,,	98·7 ,,	3½ ,,
	0·9382 ,,	99·2 ,,	4½ ,,
$H_2SO_4,12H_2O$ (No Everitt's salt left)	1·0285 ,,	75 ,,	2¾ ,,
	1·7694 ,,	81 ,,	5 ,,
	1·0912 ,,	100 ,,	6½ ,,
$H_2SO_4,14H_2O$	0·8574 ,,	47·2 ,,	1 ,,
	0·8642 ,,	57·0 ,,	2 ,,
	0·7440 ,,	65·0 ,,	3 ,,
	1·7230 ,,	80·5 ,,	3½ ,,
	1·0900 ,,	86·0 ,,	4 ,,
	0·9796 ,,	94·8 ,,	7½ ,,
$H_2SO_4,16H_2O$	1·0848 ,,	71·0 ,,	1 ,,
	2·0532 ,,	70·6 ,,	2 ,,
	0·8896 ,,	84·9 ,,	2 ,,
	1·5426 ,,	91·5 ,,	3 ,,
	1·1634 ,,	94·0 ,,	3 ,,
	0·9846 ,,	98·0 ,,	3 ,,
	0·7461 ,,	99·1 ,,	3¼ ,,
	0·9894 ,,	99·3 ,,	3½ ,,
$H_2SO_4,18H_2O$	1·0766 ,,	98·7 ,,	2½ ,,
	1·1212 ,,	98·2 ,,	2 ,,
	0·7394 ,,	99·0 ,,	2 ,,

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* A number of experiments were made to see if formic acid could be prepared in quantity by modifying the action of $H_2SO_4,4H_2O$ on potassium ferrocyanide, with, however, no satisfactory results.

hardly any carbon monoxide being obtained. Thus, 0·57 gram of potassium ferrocyanide heated for one hour with a large excess of $H_2SO_4,6H_2O$ in an atmosphere of carbon dioxide, gave less than 0·5 c.c. of carbon monoxide. The reaction began at about 120°.

The table on p. 154 contains a summary of the results obtained, using as nearly as possible the same weight of potassium ferrocyanide and a large excess of sulphuric acid, so as to keep the concentration of the acid nearly constant. The reaction in every case was carried out in an atmosphere of hydrogen as far as possible free from air. In all cases, traces of formic acid could be detected.

These results show that the theoretical yield of hydrocyanic acid was obtained by using acid of a concentration not exceeding that represented by $H_2SO_4,10H_2O$.

At first, difficulty was experienced in obtaining consistent results. This was found to be due to

(1) The rate at which the mixture was boiled.

(2) The presence of traces of air.

(3) The mass of potassium ferrocyanide used, the mass of acid being kept constant.

The effect due to the first cause is seen in the preceding table, by comparing, for example, the results obtained with $H_2SO_4,10H_2O$ and $H_2SO_4,14H_2O$ respectively. The mixture was boiled much more rapidly in the case of the former.

The effect of the second cause is seen in the following table containing the results of experiments in which a very slow stream of air was used :

Acid.	$K_4Fe(CN)_6$.	HCN [calc. as 6HCN per mol. $K_4Fe(CN)_6$].	Time.
$H_2SO_4,6H_2O$	0·9432 grams.	54·5 per cent.	7 hours (air present)
	0·8088 ,,	39 ,,	6½ ,, (,, absent)
$H_2SO_4,8H_2O$	0·9770 ,,	61·2 ,,	4½ ,, (,, present)
	1·1114 ,,	47 ,,	3 ,, (,, absent)
$H_2SO_4,14H_2O$	1·9992 ,,	71·2 ,,	3 ,, (,, present)
	1·1031 ,,	75·2 ,,	3 ,, (,, ,,)
	0·7793 ,,	98·1 ,,	4 ,, (,, ,,)
	0·7440 ,,	65 ,,	3 ,, (,, absent)

The influence of the third cause, namely, that of mass, is seen in the following table, and becomes less with increasing dilution of the acid :

Acid.	$K_4Fe(CN)_6$.	HCN [calc. as 6HCN per mol. $K_4Fe(CN)_6$].	Time.
$H_2SO_4,8H_2O$	2·2074 grams.	24·5 per cent.	2 hours.
	0·8463 ,,	36·6 ,,	2 ,,
$H_2SO_4,12H_2O$	2·2826 ,,	60·2 ,,	3 ,,
	2·1354 ,,	66·6 ,,	3½ ,,
	1·6285 ,,	75·5 ,,	2¾ ,,
$H_2SO_4,16H_2O$	2·0552 ,,	70·6 ,,	2 ,,
	0·8896 ,,	84·9 ,,	2 ,,
	1·5426 ,,	91·5 ,,	3 ,,
	0·9846 ,,	98·3 ,,	3 ,,
$H_2SO_4,18H_2O$	1·1212 ,,	98·2 ,,	2 ,,
	0·7394 ,,	99·0 ,,	2 ,,

Explanation of the Reaction.

The reaction is probably explained in the following way. Hydroferrocyanic acid is first obtained, and can be isolated and examined. With strong sulphuric acid, it decomposes very slowly, evolving carbon monoxide, and forming ferrous and ferric sulphates, &c.

With an acid of the concentration $H_2SO_4,2H_2O$, it decomposes quantitatively, forming carbon monoxide and ferrous, &c., sulphates. With sulphuric acid of less concentration, the following reactions occur.

(i) The hydroferrocyanic acid reacts with the potassium sulphate, forming Everitt's salt (Aschoff, *loc. cit.*):

$$2H_4Fe(CN)_6 + 2K_2SO_4 = 2KHSO_4 + 6HCN + K_2Fe_2(CN)_6.$$

(ii) At the same time, the hydroferrocyanic acid decomposes, forming $FeSO_4$ and HCN.

$$H_4Fe(CN)_6 = 4HCN + Fe(CN)_2.$$
$$Fe(CN)_2 + H_2SO_4 = FeSO_4 + 2HCN.$$

This second reaction becomes more marked the greater the dilution, and predominates with an acid of the concentration $H_2SO_4,10H_2O$, or with more dilute acids.

The second mode of decomposition explains the fact that with, for example, $H_2SO_4,18H_2O$, the whole of the cyanogen is evolved as hydrocyanic acid rapidly and completely. If Everitt's salt were formed, the decomposition would take much longer, as this compound is only slowly decomposed by acid of this composition.

Interaction of Hydroferrocyanic Acid and Potassium Sulphate.

In order to investigate the reaction between hydroferrocyanic acid and potassium sulphate, aqueous solutions of varying strengths of hydroferrocyanic acid were boiled with potassium sulphate solution in an atmosphere of hydrogen, a double surface condenser being used to keep the concentration constant. The water used had been boiled and also cooled in hydrogen to remove dissolved air.

In one case, a 10 per cent. solution of hydroferrocyanic acid with excess of potassium sulphate gave a precipitate of Everitt's salt on boiling. On warming the precipitate with dilute sulphuric acid at 60° * and filtering, no ferrous sulphate was found in the filtrate, hence no ferrous cyanide was formed.

A 0·7 per cent. solution of hydroferrocyanic acid was similarly treated, and a precipitate obtained. It was, however, merely ferrous cyanide, as it rapidly and completely dissolved in dilute sulphuric acid at 60°, forming ferrous sulphate and evolving hydrocyanic acid.

The precipitate obtained from the strong (10 per cent.) solution was collected in absence of air, washed repeatedly, placed in a desiccator in an atmosphere of carbon dioxide, and dried in a vacuum at 100° over phosphoric oxide. The pale bluish-yellow precipitate contained potassium, iron, and cyanogen, and was analysed by (i) evaporating down with strong sulphuric acid and a little ammonium sulphate and igniting; (ii) boiling with mercuric oxide, filtering, igniting, and weighing as ferric oxide.

0·3086 gave 0·1457 Fe_2O_3. Fe = 33·1.

$K_2Fe_2(CN)_6$ requires Fe = 32·4 per cent.

Decomposition of Hydroferrocyanic Acid.

A number of experiments were made with the object of studying the decomposition represented by the equation:

$$H_4Fe(CN)_6 = Fe(CN)_2 + 4HCN.$$
$$Fe(CN)_2 + H_2SO_4 = FeSO_4 + 2HCN.$$

According to Berzelius (*loc. cit.*) the decomposition with boiling water is represented by the equation:

$$H_4Fe(CN)_6 = 4HCN + Fe(CN)_2.$$

Reemann and Carius (*Annalen*, 1860, **113**, 39), and Étard and Bémont, (*Compt. rend.*, 1884, **99**, 1024), on the other hand, express it by the equation:

$$2H_4Fe(CN)_6 = 6HCN + H_2Fe_2(CN)_6,$$

but, in their papers, give neither analyses nor details.

To examine this question, a quantity of hydroferrocyanic acid was prepared by Possell's method, and purified by repeatedly dissolving in absolute alcohol and reprecipitating by ether until spectroscopically

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* Ferrous cyanide dissolves completely and rapidly at 60° in dilute sulphuric acid.

free from potassium. After drying in a vacuum over phosphoric oxide at 60°, this was analysed. Determination of the iron gave:

	I.	II.	III.	Calc.
Fe	25·8	26·0	25·85	26·04 per cent.

On heating with water in an atmosphere of hydrogen, hydrocyanic acid began to be evolved at 60°, and a pale yellow-green solid separated out, thus proving Berzelius' statement to be correct. The hydrocyanic acid evolved was estimated as above.

0·4970 $H_4Fe(CN)_6$ gave 0·2605 HCN. HCN = 52·4.
0·3863 $H_4Fe(CN)_6$,, 0·2035 HCN. HCN = 52·7.
3HCN requires 37·5 per cent. 4HCN requires 50 per cent.

The excess of hydrocyanic acid is undoubtedly due to hydrolysis of the ferrous cyanide, as on further boiling hydrocyanic acid is slowly evolved, and the precipitate, after drying in a vacuum, was found to contain ferrous oxide.

In presence of air, a coppery-blue precipitate was formed, but in too small a quantity for analysis. It was undoubtedly Williamson's blue, $KFe_2(CN)_6$, as this is formed from Everitt's salt in presence of air and sulphuric acid (Williamson, *loc. cit.*). That Everitt's salt in presence of air is converted more or less completely to Williamson's blue, which, in the presence of dilute acid and oxygen, decomposes as fast as it is formed, was confirmed by preparing a quantity of the latter. On boiling this with dilute sulphuric acid in presence of air it dissolved, forming hydrocyanic acid and ferric sulphate.

$$2KFe_2(CN)_6 + 8H_2SO_4 + O = 2KHSO_4 + Fe_2(SO_4)_3 + H_2O + 12HCN.$$

Summary.

The preceding results may be epitomised:

(i) Concentrated sulphuric acid, H_2SO_4, dissolves potassium ferrocyanide and shares the potassium with the hydroferrocyanic acid. The ratio must be primarily determined by the active masses and relative affinities of the acids. The following equation represents the initial change:

$$K_4Fe(CN)_6 + H_2SO_4 = 4KHSO_4 + H_4Fe(CN)_6.$$

The solution is only very slowly decomposed by rise of temperature. Carbon monoxide is given off, but even at 200° the rate of evolution is low and the decomposition proceeds only when the sulphuric acid can dissociate or decompose into water, sulphur trioxide, and sulphur dioxide.

(ii) With the addition of water, marked decomposition occurs, and large quantities of carbon monoxide are formed. This reaction increases with dilution until the concentration $H_2SO_4,2H_2O$ is reached;

at this strength, the whole of the cyanogen appears as carbon monoxide at 180°. The equation which represents this change is:

$$K_4Fe(CN)_6 + 8(H_2SO_4,2H_2O) = 4KHSO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO + 10H_2O.$$

In this case, there is evidently hydrolysis, and it seems probable that it may be directly due to the molecules of water which are dissociated by solution in the solvent H_2SO_4. On the other hand, it is possible that sulphuric acid of the concentration $H_2SO_4,2H_2O$ may really act as orthosulphuric acid, $S(OH)_6$, in which case the above reaction may be evidence of its existence.

(iii) With further dilution to the concentration $H_2SO_4,4H_2O$ there is another definite change in the reaction, since, in addition to carbon monoxide, Everitt's salt, $K_2Fe_2(CN)_6$, and hydrocyanic acid make their appearance. That this is a definite change is shown by the fact that warm acid of the strength $H_2SO_4,2H_2O$ immediately decomposes Everitt's salt.

The Everitt's salt appears to be formed from hydroferrocyanic acid by the action of potassium sulphate solution, thus:

$$2H_4Fe(CN)_6Aq + 2K_2SO_4Aq = K_2Fe_2(CN)_6 + 2KHSO_4Aq + 6HCNAq.$$

Some hydroferrocyanic acid is decomposed at the same time, forming hydrogen cyanide and ferrous cyanide. With increasing dilution, this becomes the more important and eventually, with acid of the concentration $H_2SO_4,10H_2O$, the sole reaction. The equation which may represent this stage is:

$$H_4Fe(CN)_6Aq = 4HCNAq + Fe(CN)_2.$$

In presence of the sulphuric acid, the ferrous cyanide dissolves with the formation of ferrous sulphate and hydrocyanic acid, and the change as a whole may be considered as due to the molecules of sulphuric acid dissociated by solution in the solvent water.

The final equation now becomes:

$$K_4Fe(CN)_6 + 5(H_2SO_4,10H_2O) = 4KHSO_4 + FeSO_4 + 6HCN + 50H_2O.$$

(iv) The final decomposition is hindered by increasing the mass of the salt, but helped by increase of temperature and the presence of air.

This last condition is important, and assists in the rapid decomposition of the salt. It also explains the use of porous brick or the passage of an air current to assist in the preparation of hydrocyanic acid on the manufacturing scale.

When air is present, Williamson's blue, $KFe_2(CN)_6$, is formed in small quantity, and the solution contains ferric salts; it is probably formed from Everitt's salt, and then decomposed by the action of the oxygen of the air, as explained above.

These results, therefore, confirm the oldest account of the hydrolysis of hydroferrocyanic acid, namely, that due to Berzelius (*loc. cit.*).

The authors are engaged in further investigations of changes of the character of that described under (ii) produced by sulphuric acid, to see if they admit of further elucidation.

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