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# CLXXI.—The Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid.

By HENRY BASSETT and ALEXANDER STEVEN CORBET.

I. Potassium Ferricyanide.

THE hydrolysis of potassium ferrocyanide by dilute and by concentrated sulphuric acid follows the equations :

 $\begin{array}{l} 2{\rm K_4Fe(CN)_6} + 3{\rm H_2SO_4} = 3{\rm K_2SO_4} + {\rm K_2Fe[Fe(CN)_6]} + 6{\rm HCN} \\ {\rm K_4Fe(CN)_6} + 6{\rm H_2SO_4} + 6{\rm H_2O} = \\ 2{\rm K_2SO_4} + 3({\rm NH_4})_2{\rm SO_4} + {\rm FeSO_4} + 6{\rm CO}, \end{array}$ 

and in text-books it is presumed that similar reactions take place in the case of potassium ferricyanide :

 $\begin{array}{l} 2\mathrm{K_3Fe(CN)_6} + 6\mathrm{H_2SO_4} = 3\mathrm{K_2SO_4} + \mathrm{Fe_2(SO_4)_3} + 12\mathrm{HCN} \\ 2\mathrm{K_3Fe(CN)_6} + 12\mathrm{H_2SO_4} + 12\mathrm{H_2O} = \\ 3\mathrm{K_2SO_4} + 6(\mathrm{NH_4)_2SO_4} + \mathrm{Fe_2(SO_4)_3} + 12\mathrm{CO}. \end{array}$ 

Little attention appears to have been directed to the latter reactions, and apparently Williamson (Annalen, 1846, 57, 243) was the only chemist to give the subject any serious consideration. His work, however, was chiefly concerned with the ultimate analysis of the complex cyanides of iron, and the action of concentrated sulphuric acid on potassium ferricyanide was studied only in a qualitative manner. The fact that carbon dioxide appears as an end-product in the reaction apparently escaped observation entirely.

In the present investigation, a series of experiments was carried out in which potassium ferricyanide was warmed with sulphuric acid of varying concentrations and the proportions of the endproducts obtained were quantitatively determined.

On first warming the ferricyanide with concentrated sulphuric acid a greenish-white precipitate was obtained, the colour of which varied considerably with the concentration of the acid. The nature of this precipitate was not investigated, but presumably it was hydroferricyanic acid or an acid salt of that compound. On further warming, the precipitate turned slightly blue and eventually disappeared, a clear yellowish-green solution being produced. The time of heating required for this change increased as the concentration of the sulphuric acid used was diminished. It was at the stage in the reaction when the solution was clearing that the greater part of the carbon monoxide was evolved.

We have found that when potassium ferricyanide is hydrolysed with excess of sulphuric acid some ferrous salt is invariably formed.

Using 90 per cent. (by weight) sulphuric acid, the hydrolysis could

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not be completed, but with about 80 per cent. sulphuric acid almost the whole of the ferric salt was reduced, whilst one-twelfth of the earbon monoxide was oxidised to carbon dioxide. In this case, the completed reaction was represented by the equation

# $\begin{array}{l} 2\mathrm{K_3Fe(CN)_6} + 11\mathrm{H_2SO_4} + 13\mathrm{H_2O} = \\ 3\mathrm{K_2SO_4} + 6(\mathrm{NH_4})_2\mathrm{SO_4} + 2\mathrm{FeSO_4} + 11\mathrm{CO} + \mathrm{CO_2}. \end{array}$

On using more dilute sulphuric acid, a diminution in the yield of oxides of carbon and ferrous sulphate resulted, with a corresponding increase in the hydrocyanic acid and ferric sulphate formed. In fact, the reaction tended more and more to follow the equation

 $2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN.$ 

When the concentration of the sulphuric acid was not above 30 per cent., the hydrolysis took much longer than previously, and the carbon finally appeared almost wholly as hydrocyanic acid. With acid of this concentration, a yellowish-green solution was obtained which persisted for some time, eventually turning very dark and finally clearing to give a straw-coloured solution. At this stage, the oxides of carbon were evolved in such small amounts that determinations were scarcely practicable.

With any given concentration of sulphuric acid, the proportions of the end-products were not quite constant, but appeared to depend to some extent on the manner in which the mixture was heated. This was to be expected, as in all cases water distilled over, causing the acid solution to become more concentrated as heating was continued.

In general, the course of the reaction appears to be similar to that between potassium ferrocyanide and sulphuric acid. The hydroferricyanic acid (or acid salt) first liberated is hydrolysed to potassium sulphate, ferric sulphate, and hydrocyanic acid, and in presence of dilute acid the reaction goes no farther and hydrocyanic acid distils over. With more concentrated acid, however, some or all of the hydrocyanic acid is converted into formic acid and ultimately carbon monoxide. Some or all of the ferric salt is reduced by the formic acid with formation of a corresponding amount of carbon dioxide, and the extent to which this occurs depends on the concentration of the sulphuric acid.

That the formic acid is the reducing agent appears probable from experiments in which ferric alum and formic acid were heated together in presence of sulphuric acid in quantities which made the conditions comparable with those of the reaction under consideration. In these experiments, it was found that the formic acid was able to reduce the ferric salt present.

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Under conditions which prevailed during the experiments, carbon monoxide had no reducing action on ferric salts in presence of sulphuric acid.

It is well known that aqueous solutions of potassium ferricyanide decompose comparatively quickly when exposed to light and Vogel (Ber., 1871, 4, 90) first showed that the formation of ferrocyanide in solutions of ferricyanide on standing is due to the action of light and not to dust particles. The nature of this photochemical change, however, does not appear to have been fully investigated. Some reduction of ferric to ferrous iron certainly occurs which leads to the formation of blue complex ferri-ferrocyanides, but it seems more than doubtful whether the reduction mechanism is the same as that operating under the conditions we have examined. In the light reaction, it may well be that ferric ions oxidise cyanide ions to cyanogen in spite of the fact that there is only a very low concentration of either of these ions in a solution of potassium ferricyanide. The reaction would then be analogous to the oxidation of cyanide by cupric or thallic salts and the possibility of this same mechanism prevailing during the hydrolysis of potassium ferricyanide by sulphuric acid is not entirely excluded. It seems incapable of proof, however, and unlikely from the fact that the proportion of ferric ions reduced increased with the concentration of the acid. Concentrated acid solutions would not be favourable to the existence of evanide-ions owing to hydrocyanic acid being so weak.

#### EXPERIMENTAL.

The purity of the potassium ferricyanide used could not be accurately ascertained by means of potassium permanganate, and was eventually determined by Müller and Diefenthäler's modification of Lenssen's method (Annalen, 1854, 91, 240). The faintly acid solution of the ferricyanide was treated with potassium iodide and pure zinc sulphate; iodine was liberated, whilst the ferrocyanide formed was precipitated as zinc ferrocyanide. The free iodine was titrated against sodium thiosulphate, with starch as indicator. The material was thus found to contain 99.6 per cept. of potassium ferricyanide. The purity was further checked by a determination of the total nitrogen present as hydrocyanic acid and ammonia after hydrolysis.

For each experiment, about 0.05 to 0.1 gram of potassium ferricyanide was weighed into a distilling flask, which was connected with a Schiff's nitrometer containing strong potassium hydroxide solution, prepared from boiled water and saturated with carbon monoxide before use (carbon monoxide was sufficiently soluble in

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strong potassium hydroxide solution to affect the results). Dry carbon dioxide from a Farmer apparatus (J., 1920, 117, 1446) was used to displace the air and to drive over any carbon monoxide remaining in the distilling flask on the completion of the hydrolysis. The sulphuric acid used for the experiments was boiled to expel air, cooled in a current of carbon dioxide, and introduced into the flask by means of a tap-funnel. (The strength of the sulphuric acid was first determined by titration with standard alkali, but later it was found that hydrometers were sufficiently accurate for the purpose.) The mixture was heated to boiling while the current of carbon dioxide carried the carbon monoxide evolved to the nitrometer. On completion of the hydrolysis the carbon dioxide was passed for some time to ensure all the carbon monoxide being collected.

The residual solution in the distilling flask was diluted and the ferrous salt present titrated with 0.1N-potassium permanganate solution. This incidentally gave the carbon monoxide oxidised to dioxide. After the titration, the same solution was used to estimate the ammonia present (Kjeldahl's method).

It was found to be advisable to estimate the hydrocyanic acid and carbon dioxide in separate experiments. For determinations of the hydrocyanic acid, the aqueous distillate was absorbed in dilute potassium hydroxide contained in a flask interposed between the distilling flask and nitrometer. After hydrolysis, the contents of the flask were titrated against 0.1N-silver nitrate.

Some difficulty was experienced in the direct estimation of the carbon dioxide. In this case, the hydrolysis with sulphuric acid was carried out in a current of dry, carbon dioxide-free air, and any carbon dioxide formed was absorbed in 0.1N-sodium hydroxide solution contained in a series of boiling tubes. On completion of the hydrolysis, 10 c.c. of barium chloride solution were added to each of the tubes and the contents were titrated against standard acid with phenolphthalein as indicator.

The difficulty of this estimation lay in the fact that only a small amount of carbon dioxide was obtained with dilute sulphuric acid, but when the maximum yield was obtained with concentrated sulphuric acid there was the danger of acid coming over in the distillate at the close of the hydrolysis. However, with care, it was possible to prevent this and show that the amount of carbon dioxide obtained was the same as that calculated from the permanganate titrations of the ferrous salt.

The results obtained are given in the table and plotted in the diagram.





Table Showing Distribution of Carbon Atoms after Hydrolysis of2 Mols. of Potassium Ferricyanide.

Initial				Initial			
conc. of	CO	$CO_{2}(KMnO_{4})$	HCN	conc. of	CO	CO <sub>2</sub> (KMnO <sub>4</sub> )	HCN
H <sub>2</sub> SO <sub>4</sub> %.	(mols.).	. (mols.).	(mols.).	H <sub>2</sub> SO <sub>4</sub> %.	(mols.	). (mols.).	(mols.)
9.47		0.09	11.94	60	9.54	0.85	
18.96		0.05	11.68		9.96	0.86	
$29 \cdot 21$		0.04	11.08		10.19	0.88	
		0.05	11.26	,,	10.33	0.79	
30.48			11.11	,,,	10.46	0.79	
30.77	0.59	0.12		61.35			0.41
39.85	0.91	0.18	9.89				0.48
	1.39	0.21	9.83	63.85		0.89	
40.06			10.69	67.59			1.71
46.94	5.51			70	10.34	0.85	
48			5.11		10.61	0.92	
49.96	6.56	0.62		,,	10.62	0.83	
	6.99	0.66		70.67	10.67	0.91	
50		0.58		71.10	10.01	0.79	
		0.59		77.6		0.93	
56.38	8.39		3.56	*		0.94	
58.28			0.75	80	10.71	1.12	
			0.97		10.88	0.91	
,,			0.98	,,	11.12	1.01	
60	9.12	0.71		81.56		0.90	
"	9.32	0.81					
Tuitial area		80.0/			e	79.0 7	7.0*
Mala f CO	$\cdot$ or $\mathbf{H}_2$	5U4 %	. /1.10		0	72.0 7	1.01
MOIS, OI UU	$J_2$ (direc	C)	. 0.84	e 1.0	ವ	0.75	0.94

## II. Potassium Cobalticyanide.

The action of sulphuric acid on potassium cobalticyanide was described by Gmelin, who first prepared it ("Handbook of Chemistry," 1852, VII, 493). His observations, however, were of a purely qualitative nature, and he did not record that carbon monoxide and carbon dioxide are among the products of hydrolysis.

It was anticipated that the decomposition of potassium cobalticyanide by sulphuric acid would differ from that of potassium ferricyanide only in that a constant amount of carbon dioxide would be evolved, irrespective of the concentration of the sulphuric acid used. This should follow from the fact that all the cobalt present would appear finally as cobaltous sulphate. It was found, however, that the complete decomposition of the cobalticyanide was much more difficult to achieve than that of the ferricyanide.

When the cobalticyanide was first warmed with sulphuric acid of initial concentration about 80 per cent. (by weight), a white precipitate was thrown down, which, presumably, was hydrocobalticyanic acid; further warming gave a pink turbid solution which eventually cleared. With acid of this initial concentration, scarcely any hydrocyanic acid was obtained and the reaction followed the equation

 $2K_{3}Co(CN)_{6} + 11H_{2}SO_{4} + 13H_{2}O =$ 

 $3K_2SO_4 + 6(NH_4)_2SO_4 + 2CoSO_4 + 11CO + CO_2$ in analogy with the ferricyanide hydrolysis by sulphuric acid of this concentration. On using more dilute sulphuric acid for the hydrolysis, the same colour changes were observed, but hydrocyanic acid began to appear among the end-products in increasing amount. After heating for a short time with sulphuric acid of concentration not above 30 per cent., a bright yellow solution was obtained which became turbid on further warming, but finally cleared to give a pink solution. When the initial concentration of the acid was below 30 per cent. the proportions of the end-products were practically constant, but only about one-third of the theoretical yield of hydrocyanic acid was obtained.

It was thought that this might be due to the fact that potassium cobalticyanide is more stable than the corresponding ferricyanide, and therefore a longer time is required for complete decomposition. Under the conditions prevailing during the experiments, water distilled over during the warming and the acid became more and more concentrated. The cobalticyanide being only slowly decomposed by the dilute acid, the latter became concentrated before the decomposition was more than about one-third completed, and so the cobalticyanide was eventually hydrolysed by concentrated acid.

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To test this view, an experiment was carried out in which potassium cobalticyanide was hydrolysed by 29.84 per cent. sulphuric acid, and the mixture distilled under reflux until hydrocyanic acid ceased to be evolved. The solution became lemon-yellow on first warming, but straw-coloured as hydrolysis proceeded. It was not possible to complete the hydrolysis in one heating, but the experiment was continued for varying periods for four days, during which the hydrocyanic acid in the distillate was estimated from time to time by titration with silver nitrate. In this way, nearly  $\frac{11}{12}$  of the carbon atoms finally appeared as hydrocyanic acid, showing that under these conditions the reaction tended to follow the equation

 $\begin{array}{l} 2\mathrm{K_{3}Co(CN)_{6}+6H_{2}SO_{4}+2H_{2}O}=\\ 3\mathrm{K_{2}SO_{4}+2CoSO_{4}+(NH_{4})HSO_{4}+11HCN+CO_{2}.} \end{array}$ 

Molecules of Hydrocyanic Acid obtained by Hydrolysis of 2 Mols. of Potassium Cobalticyanide under a Reflux Condenser. Con centration of Sulphuric Acid = 29.84 per cent.

 Time (hours)
 5.75
 8.75
 10.75
 17.75
 20.50
 28.75
 31.25
 35.25

 Mols. of HCN
 6.46
 7.20
 8.12
 9.04
 9.59
 10.14
 10.32
 10.32

#### EXPERIMENTAL.

An attempt was made to determine the purity of the potassium cobalticyanide by Braun's method (Z. Chem., 1866, 2, 283) of titrating with silver nitrate in presence of potassium chromate, but this did not yield satisfactory results. The purity was found to be 99.24 per cent. by an estimation of the ammonia and hydrocyanic acid produced on decomposition with 47 per cent. sulphuric acid.

The experiments were carried out as in the case of the ferricyanide. The determinations were practically confined to hydrocyanic acid, but a few estimations of carbon dioxide also were made. The results are tabulated and represented graphically, the carbon monoxide being obtained by difference.

Distribution of Carbon Atoms after Hydrolysis of 2 Mols. of Potassium Cobalticyanide. a =initial conc. of sulphuric acid per cent.

It must be emphasised that the figures in the top row give the initial concentration of sulphuric acid. Owing to the slowness of the reaction and distillation of water hydrolysis mostly takes place after considerable concentration has occurred. There is thus no the treation of a.

# Potassium Aquopentacyanocobaltiate.

It is probable that the hydrolysis of complex cyanides occurs in a series of relatively simple steps. Some of these may involve replacement of cyanogen groups by  $H_2O$ . Some evidence for the intermediate formation of such aquo-compounds in the case of the hydrolysis of potassium cobalticyanide has been obtained. Potassium cobalticyanide was warmed with 30 per cent. sulphuric acid until a deep yellow solution was formed. This was rapidly cooled and neutralised with potassium carbonate. On evaporation in a vacuum and removal of the sulphates, which crystallised first, a white, crystalline substance was finally obtained. Analysis of this gave figures approaching those required by a potassium aquopentacyanocobaltiate 3K<sub>3</sub>Co(CN)<sub>6</sub>,K<sub>2</sub>[Co(CN)<sub>5</sub>·H<sub>2</sub>O], similar to the aquopentacyanoferriate obtained by Briggs (J., 1920, 117, A similar product was also obtained by the action of 1026). bromine on potassium cobalticyanide under conditions such as were employed by Briggs for the ferricyanide.

#### Summary.

1. Potassium ferricyanide is hydrolysed by concentrated sulphuric acid according to the equation

$$\begin{array}{l} 2\mathrm{K_3Fe(CN)_6} + 11\mathrm{H_2SO_4} + 13\mathrm{H_2O} = \\ 3\mathrm{K_2SO_4} + 6(\mathrm{NH_4})_3\mathrm{SO_4} + 2\mathrm{FeSO_4} + 11\mathrm{CO} + \mathrm{CO_2}. \end{array}$$

The fact that ferrous sulphate and carbon dioxide appear among the end-products has not been observed previously. With more dilute acid, the reaction tends to follow the equation

$$2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN.$$

2. The hydrolysis of potassium cobalticyanide by concentrated sulphuric acid follows the equation

$$\begin{array}{l} 2K_{3}Co(CN)_{6} + 11H_{2}SO_{4} + 13H_{2}O = \\ & 3K_{2}SO_{4} + 6(NH_{4})_{2}SO_{4} + 2CoSO_{4} + 11CO + CO_{2}. \end{array}$$

With more dilute acid, hydrocyanic acid is obtained as in the case of ferricyanide, but the hydrolysis is slow owing to the greater stability of the cobalticyanide. By long digestion under reflux the amount of hydrocyanic acid obtained is that required by the equation

$$\begin{array}{l} 2\mathrm{K_{3}Co(CN)_{6}+6H_{2}SO_{4}+2H_{2}O} = \\ 3\mathrm{K_{2}SO_{4}+2CoSO_{4}+(NH_{4})HSO_{4}+11HCN+CO_{2}} \end{array}$$

3. A white compound appeared as an intermediate product of hydrolysis, and a white complex cobalticyanide was also obtained by the action of bromine on potassium cobalticyanide. These substances, which appear to be potassium aquopentacyanocobaltiates, were not fully investigated.

UNIVERSITY COLLEGE, READING.

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