XX.—*The Constitution of Hydrocyanic, Cyanic, and Cyanuric Acids.*

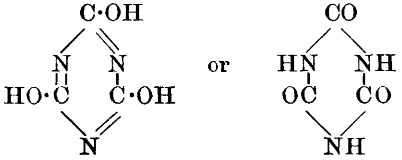
By F. D. CHATTAWAY and J. MELLO WADMORE.

ALTHOUGH the simplest cyanogen derivatives have been for more than a century among the most familiar of carbon compounds, there is no general agreement as to their constitution. They all contain a carbon and a nitrogen atom associated together, and different opinions are held as to the manner in which hydrogen or halogen atoms are attached to this group.

As a rule, well-defined classes of alkyl derivatives corresponding with each possible structure are known, the behaviour of which leaves no doubt concerning their molecular arrangement, but the reactions of the cyanogen acids, their salts and halogen derivatives, are contradictory, and apparently equally well-established facts lead to opposite conclusions.

Hydrocyanic acid, cyanogen chloride, cyanic and cyanuric acids, for example, may have the following structures:

$\mathrm{H{\cdot}C{\vdots}N}$ or $\mathrm{H{\cdot}N{:}C}$
$\mathrm{Cl{\cdot}C{\vdots}N}$ or $\mathrm{Cl{\cdot}N{:}C}$
$\mathrm{H{\cdot}O{\cdot}C{\vdots}N}$ or $\mathrm{O{:}C{\cdot}N{\cdot}H}$



The formulæ generally adopted are those given first, the hydrogen, halogen, and hydroxyl being regarded as attached to the carbon atom.

The knowledge which we have recently acquired of the strikingly different behaviour of halogen when attached to carbon or to nitrogen made it probable that a study of the action of halogens on the cyanogen acids, and of the derivatives thereby produced, would afford direct evidence as to their constitution. Speaking generally, imino-hydrogen is more readily replaced by halogen than hydrogen attached to carbon, and the imino-halogen compounds are characteristically reactive, while the carbon halogen linkage is comparatively stable.

Cyanogen chloride, bromide, and iodide were among the earliest discovered compounds of cyanogen, as they are formed with the greatest ease by the action of the halogens on aqueous solutions of hydrocyanic acid or its salts. A careful study of the behaviour of these compounds shows that they possess all the typical and characteristic properties of compounds having halogen attached to nitrogen.

They react, for example, quantitatively with solutions of hydriodic acid, sulphurous acid, and hydrogen sulphide, hydrocyanic acid being in each case reformed, while iodine, sulphuric acid, and sulphur are respectively produced.

Taking cyanogen bromide, for example, the reactions are represented by the equations:

$$C\colon N{\cdot}Br + 2HI = C\colon N{\cdot}H + HBr + I_2.$$
$$C\colon N{\cdot}Br + H_2SO_3 + H_2O = C\colon N{\cdot}H + HBr + H_2SO_4.$$
$$C\colon N{\cdot}Br + H_2S = C\colon N{\cdot}H + HBr + S.$$

This behaviour shows that the halogen is attached to nitrogen and not to carbon in these compounds, and that, consequently, they must be represented by the formulæ:

$$C\colon N{\cdot}Cl; \quad C\colon N{\cdot}Br \quad \text{and} \quad C\colon N{\cdot}I.$$

The carbon is conventionally represented as divalent, and the nitrogen as trivalent; no very different conception, however, would be expressed if the carbon were represented as tetravalent and the nitrogen as pentavalent, since what is implied is that the carbon is attached to the nitrogen by the resultant affinity which, under the circumstances, the atoms are capable of exerting.

The ease with which the cyanogen halogen compounds can be formed from prussic acid and its salts, and again transformed into them, makes it in the highest degree probable that these have the imino-constitution, and hence should be represented by the formulæ:

$$C\colon N{\cdot}H \quad C\colon N{\cdot}K \quad C\colon N{\cdot}Ag.$$

This conclusion, moreover, is the only one which will satisfactorily explain their whole chemical behaviour.*

The relations of the cyanides and cyanogen chloride to cyanic acid

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* We have not thought it necessary to go into explanatory details as these can be easily supplied.

and its salts have been among the chief reasons which led to the adoption of the hydroxy-formulæ :

$$N{:}C{\cdot}OH \qquad\qquad N{:}C{\cdot}O{\cdot}K.$$

for these compounds.

Since, as we have just shown, the former are imino-compounds these relations become reasons for adopting the alternative imino-structure :

$$O{:}C{\cdot}NH \quad \text{and} \quad O{:}C{:}N{\cdot}K.$$

For example, the production of potassium cyanate, when cyanogen chloride is treated with aqueous potash, has been used as an argument for the hydroxy-constitution, since if the chlorine in cyanogen chloride is attached to carbon, it could be regarded as a normal case of hydrolysis :

$$N{:}C{\cdot}Cl + 2KOH = KCl + N{:}C{\cdot}O{\cdot}K + H_2O.$$

Cyanogen chloride, however, has the imino-structure, and the reaction becomes an argument in the other direction, for a comparison of this behaviour with that of the analogous cyanogen iodide shows that it must be regarded as a normal hydrolysis of a nitrogen chloride followed by oxidation of the potassium cyanide first formed :

$$\begin{aligned} C{:}N{\cdot}Cl + 2KOH &= C{:}N{\cdot}K + KOCl + H_2O. \\ &= O{:}C{:}N{\cdot}K + KCl + H_2O. \end{aligned}$$

Analogy with cyanuric acid also is in favour of the imino-structure.

The action of chlorine on a solution of potassium cyanurate is precisely similar to its action on potassium cyanide, the potassium atoms are replaced by chlorine, and a well-defined crystalline compound is produced, thus :

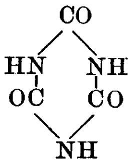
$$C_3K_3N_3O_3 + 3Cl_2 = C_3Cl_3N_3O_3 + 3KCl.$$

The entire chemical behaviour of this substance shows that the whole of its halogen is attached to nitrogen. It liberates chlorine when treated with hydrochloric acid, iodine with hydriodic acid, and oxidises sulphurous to sulphuric acid. Cyanuric acid is, in each case, reformed, and the reactions are quantitative ; the action with hydrochloric acid, for example, takes place according to the equation :

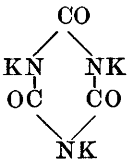
$$C_3Cl_3N_3O_3 + 3HCl = C_3H_3N_3O_3 + 3Cl_2.$$

It is hydrolysed by water or alkalis, yielding hypochlorous acid or hypochlorites. It reacts explosively with a strong ammonia solution, nitrogen being liberated, and also with a solution of hydrogen sulphide, setting free sulphur. Cyanuric acid is in each case reformed. The compound must therefore be trichloriminocyanuric acid.

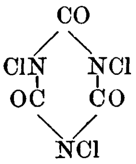
Since cyanurates are so readily and completely converted into this trichlorimino-derivative, and the latter in many reactions equally readily and completely again into cyanuric acid, we are justified in concluding that Hofmann was in error in assigning a hydroxy-constitution to the acid and its salts, and that, on the contrary, they have the imino-constitution, and assuming the correctness of the cyclic structure that they must be expressed by the formulæ



Cyanuric acid.



Potassium cyanurate.

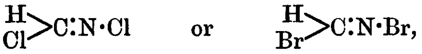


Trichlorimino-cyanuric acid.

A similar study of the behaviour of cyanuric chloride and bromide confirms Hofmann's conclusion that in them the halogen is attached to the carbon and not to the nitrogen. They do not liberate iodine from hydriodic acid or sulphur from hydrogen sulphide, nor do they oxidise sulphurous acid, even when heated to 100° with these reagents.

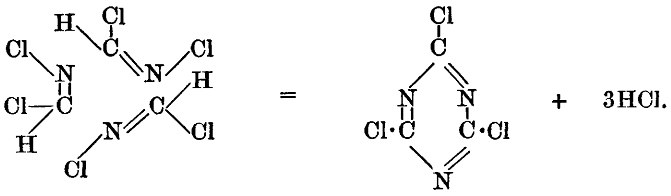
This constitution, however, was to be expected from the structure of the cyanogen halogen compounds, from which they are produced by polymerisation under the influence of halogen acids.

Cyanogen chloride and bromide, as we have shown, are chlorimino-derivatives in which the carbon being unsaturated is able to combine with two monad atoms. In the polymerisation, the halogen acid in all probability first adds itself on forming molecules having the constitution :



$$\left.\begin{matrix}H\\Cl\end{matrix}\right>C{:}N{\cdot}Cl \quad \text{or} \quad \left.\begin{matrix}H\\Br\end{matrix}\right>C{:}N{\cdot}Br,$$

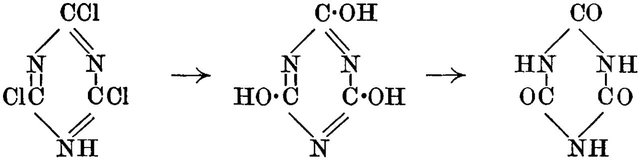
which, on coming into contact, unite into ring systems of normal structure with elimination of halogen acid, thus :



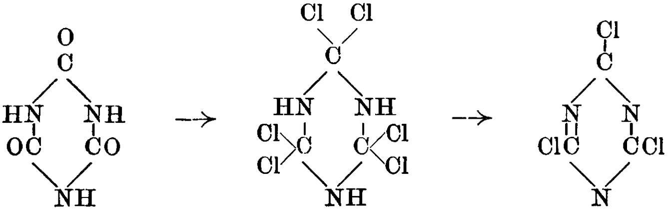
As Hofmann has pointed out, all the relations of the cyanogen group can only be explained by assuming isomeric change to occur in certain reactions ; the issue is as to where this takes place.

Cyanuric chloride, as is well known, yields cyanuric acid and hydrochloric acid on prolonged heating with water, the reaction being more rapid if alkalis are present. This and the corresponding conversion of cyanuric acid into cyanuric chloride by phosphorus pentachloride are the chief grounds on which Hofmann assigned the hydroxy-structure to the acid.

If, however, the views now put forward as to its constitution are correct, these are the reactions where isomeric change occurs, and analogous behaviour in other well-established cases renders this probable. We must assume that in the hydrolysis of cyanuric chloride normal cyanuric acid is first formed, but as in many cases where we have the grouping $-\overset{\mathrm{O\cdot H}}{\overset{|}{\mathrm{C}}}=\mathrm{C}=$, the configuration is unstable and passes into the stable arrangement $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}=$, so here we have an intramolecular change, the stable imino-form of ordinary cyanuric acid being the result:



The action of phosphorus pentachloride on cyanuric acid is probably analogous to its action on amides, the replacement of an oxygen atom by two chlorine atoms being followed by the elimination of hydrogen chloride:



EXPERIMENTAL.

Cyanogen Chloride, C:N·Cl.

This compound shows the characteristic behaviour of a nitrogen chloride, although it reacts less readily than is usual with such substances. When hydriodic acid is added to an aqueous solution of cyanogen chloride at the ordinary temperature, very little iodine is liberated; the amount, however, increases slowly on standing, rapidly on heating to near 100°, until it reaches about 80 per cent. of that required by the equation:

$$C\vdots N\cdot Cl + 2HI = C\vdots N\cdot H + HCl + I_2.$$

If the heating be prolonged, the free iodine slowly disappears, probably owing to hydrolysis of the hydrocyanic acid, and oxidation of the formic acid or ammonia produced.

When aqueous solutions of cyanogen chloride and hydrogen sulphide are heated together to 100°, sulphur is set free in considerable quantity; the hydrocyanic acid formed is mainly hydrolysed, but a small amount escapes decomposition and combines with some of the liberated sulphur to produce thiocyanic acid.

Similarly, when solutions of cyanogen chloride and sulphurous acid or sulphites are heated to 100°, the latter are oxidised while the hydrocyanic acid is destroyed, probably hydrolysed.

No liberation of chlorine can be detected when a solution of cyanogen chloride is heated with hydrochloric acid to 100°; the cyanogen chloride, however, is completely decomposed at this temperature.

The production of potassium cyanate and chloride by heating cyanogen chloride with caustic potash is probably due to the normal hydrolysis which all chlorimino-compounds undergo, followed by a subsequent oxidation of the cyanide by the hypochlorite formed.

$$C\vdots N\cdot Cl + 2KOH = C\vdots N\cdot K + KOCl + H_2O = O\colon C\colon N\cdot K + KCl + H_2O.$$

Cyanogen Bromide, $C\vdots N\cdot Br$.

Cyanogen bromide is much more reactive than cyanogen chloride. At the ordinary temperature, it liberates iodine from hydriodic acid, sulphur from hydrogen sulphide, and oxidises sulphurous acid or sodium sulphite. All these reactions are quantitative, hydrocyanic and hydrobromic acids being formed in equivalent amount.

A weighed quantity of cyanogen bromide was added to an excess of a solution of hydriodic acid made by dissolving 10 grams of potassium iodide in 100 c.c. of a 5 per cent. solution of acetic acid; hydrocyanic acid and iodine were at once liberated, the latter being then estimated by sodium thiosulphate:

0·2439 liberated I = 46 c.c. *N*/10 iodine. Br as $\vdots N\cdot Br = 75{\cdot}4$.*
$C\vdots N\cdot Br$ requires 75·43 per cent.

A weighed quantity of cyanogen bromide was added to an excess of an approximately decinormal solution of hydrogen sulphide; sulphur

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* Throughout this paper the results are calculated on the assumption that the substances under consideration react as typical nitrogen halogen compounds, the numbers are then compared with the percentages calculated from the formulæ.

was at once deposited and hydrobromic and hydrocyanic acids formed, together with a little thiocyanic acid, produced by the action of the sulphur on the latter; the excess of hydrogen sulphide was then estimated by a solution of iodine:

0·4791 reacted with 90·7 c.c. *N*/10 $H_2S/2$. Br as $\colon N\cdot Br = 75\cdot 68$.
$C\vdots N\cdot Br$ requires 75·43 per cent.

A similar procedure was adopted in studying the reaction with sulphurous acid. A weighed quantity of cyanogen bromide dissolved in dilute acetic acid was added to an excess of a decinormal solution of sodium sulphite, and then the excess of the latter estimated by a solution of iodine:

0·5050 reacted with 95·25 c.c. *N*/10 $Na_2SO_3/2$. Br as $\colon N\cdot Br = 75\cdot 41$.
$C\vdots N\cdot Br$ requires 75·43 per cent.

No bromine is liberated when cyanogen bromide is heated with a solution of potassium bromide made acid with acetic acid, or when it is heated with strong hydrochloric acid to 100°, although in the latter case it is decomposed just as cyanogen chloride is when similarly treated.

Cyanogen Iodide.

Cyanogen iodide is more reactive than cyanogen chloride or cyanogen bromide, and behaves as a typical nitrogen iodide. It reacts with hydriodic acid, liberating iodine, with hydrobromic acid liberating bromine and iodine, with hydrochloric acid forming iodine monochloride; it oxidises sulphurous acid and sodium sulphite, forming sulphates and sets free sulphur from hydrogen sulphide. Its behaviour towards several of these substances was very carefully studied by E. von Meyer (*J. pr. Chem.*, 1887, [ii], **35**, 292). He showed that the reaction between hydrocyanic acid and iodine is a reversible one, and that two molecules of sulphur dioxide completely reduce two molecules of cyanogen iodide to hydrocyanic and hydriodic acids. He, however, writes the formula ICN, and concludes his paper by stating that it is the only oxygen-free iodide soluble in water which shows the surprising behaviour of liberating iodine under the action of reducing agents, but of remaining unattacked by reagents which set iodine free from other iodides.

We have quantitatively studied the behaviour of cyanogen iodide in order to compare it with that of the bromide and the chloride. A weighed quantity of cyanogen iodide was added to an excess of a solution of 10 grams of potassium iodide in 5 per cent. acetic acid; hydrocyanic acid and iodine were at once liberated, the amount of the latter being then estimated by sodium thiosulphate:

0·2964 liberated I = 38·8 c.c. *N*/10 iodine. I as $\colon N\cdot I = 83\cdot 02$.
$C\vdots N\cdot I$ requires 82·97 per cent.

This result is exactly that required by the equation :

$$C\colon N\cdot I + HI = C\colon N\cdot H + I_2.$$

When cyanogen iodide is dissolved in an excess of strong hydrochloric acid at the ordinary temperature, very little action takes place, but on warming to 20—30° the liquid becomes orange-coloured, owing to the formation of iodine monochloride, and the colour deepens as the temperature rises. There is no liberation of free iodine even on boiling the solution. Hydrocyanic acid is also produced. In one experiment, the iodine monochloride was distilled off into a solution of potassium iodide, and the liberated iodine estimated. The amount of iodine monochloride obtained was about 2 per cent. below that required by the equation

$$C\colon N\cdot I + HCl = C\colon N\cdot H + ICl.$$

The loss is probably due to the hydrolysis of a small amount of the hydrocyanic acid and partial oxidation by the iodine monochloride of the products.

When cyanogen iodide is similarly treated with hydrobromic acid, both iodine and bromine are evolved, but, as with hydrochloric acid, the amount falls somewhat short of that required by the equation

$$C\colon N\cdot I + HBr = C\colon N\cdot H + BrI,$$

probably from a similar cause.

When a solution of sulphurous acid is slowly added to cyanogen iodide, iodine is liberated, hydrocyanic acid and sulphuric acid being simultaneously formed ; if, however, the iodide be added to an excess of sulphurous acid, no liberation of halogen occurs (compare Strecker, *Annalen*, 1868, **148**, 90).

A weighed quantity of cyanogen iodide was added to an excess of a decinormal solution of sodium sulphite so that no iodine was set free, and the excess of sulphite estimated by a dilute solution of iodine :

0·2960 oxidised 38·7 c.c. of $N/10$ $Na_2SO_3/2$. I as $\colon N\cdot I = 82\cdot92$.
$C\colon N\cdot I$ requires 82·97 per cent.

The action takes place according to the equation

$$2C\colon N\cdot I + H_2SO_3 + H_2O = 2C\colon N\cdot H + H_2SO_4.$$

Sulphur is set free and hydrocyanic and hydriodic acids are formed when cyanogen iodide is added to an excess of a solution of hydrogen sulphide. If the latter is slowly added to the iodide, iodine is also liberated, owing to the action of the hydriodic acid first formed on the unchanged cyanogen iodide. A little thiocyanic acid also is always formed from the interaction of some of the hydrocyanic acid with the sulphur.

In the following experiment, cyanogen iodide was added to an excess of hydrogen sulphide, the amount of the latter remaining unacted on being estimated by a solution of iodine:

0·2896 reacted with 37·9 c.c. *N*/10 $H_2S/2$. I as $\vdots N \cdot I = 83$.
$C \vdots N \cdot I$ requires 82·97 per cent.

The result is expressed by the equation

$$2C \vdots N \cdot I + H_2S = 2C \vdots N \cdot H + 2HI + S.$$

Its behaviour towards a solution of potassium hydrate also shows that in it the halogen is attached to nitrogen, and affords an explanation of the apparently different action of the similarly constituted cyanogen chloride and bromide.

When it is added to a boiling solution of caustic potash, it is at once decomposed; among other products, a small quantity of potassium iodate is formed. Cyanogen chloride and bromide, when similarly treated, form no chlorate or bromate. All the cyanogen halogen compounds, however, are readily decomposed by caustic alkalis, yielding cyanates.

The nitrogen halogen linkage, as is well known, behaves in a characteristic way on hydrolysis, the halogen being invariably replaced by hydrogen and becoming itself attached to the residual hydroxyl, thus:

$$\cdot N \cdot X + H \cdot O \cdot H = \cdot N \cdot H + X \cdot O \cdot H.$$

It is thus sharply distinguished from the carbon halogen linkage, where the opposite happens, thus:

$$\cdot C \cdot X + H \cdot O \cdot H = \cdot C \cdot O \cdot H + XH.$$

The formation of iodate in the reaction between cyanogen iodide and potash shows that, at first, nitrogen halogen hydrolysis undoubtedly takes place, thus:

$$C \vdots N \cdot I + 2KOH = C \vdots N \cdot K + K \cdot O \cdot I + H_2O.$$

A certain amount of the hypoiodite, on account of the ease with which it is transformed into iodide and iodate, escapes reduction by the cyanide simultaneously formed, a reaction which results in the production of cyanate:

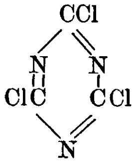
$$C \vdots N \cdot K + K \cdot O \cdot I = O \colon C \cdot N \cdot K + KI.$$

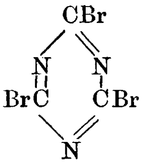
In the cases of cyanogen chloride and bromide, the hypochlorite and hypobromite, which must first be formed, do not transform so readily, and consequently are wholly reduced.

Cyanuric Chloride and Bromide.

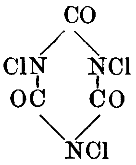
These compounds show none of the reactions characteristic of the halogen nitrogen linkage.

Small quantities of each were taken and heated for 30 minutes at 100° in stoppered bottles, air being excluded, with solutions of hydriodic acid, hydrogen sulphide, and sodium sulphite. No iodine or sulphur was liberated, nor was the sulphite oxidised. This behaviour is in agreement with Hofmann's view of their constitution, deduced from altogether different reactions, and with the formula assigned to them by him and generally adopted :





Trichloriminocyanuric Acid,



This compound is prepared with the greatest ease by dissolving cyanuric acid in the theoretical quantity of a 5 per cent. solution of caustic potash and passing a rapid stream of chlorine through the liquid cooled to 0°.

Trichloriminocyanuric acid separates as a heavy, white, crystalline powder which is obtained perfectly pure by washing a few times with water and drying rapidly on a water-bath :

$$O_3C_3N_3K_3 + 3Cl_2 = O_3C_3N_3Cl_3 + 3KCl.$$

Using about 3 grams of acid, a yield of more than 90 per cent. of the theoretical is obtained. If a larger quantity than this be used or the temperature be allowed to rise, the yield is much diminished and the product is more or less impure.

Trichloriminocyanuric acid is a white, crystalline powder which, under the microscope, is seen to consist of short prisms. It has a characteristic odour resembling that of hypochlorous acid. It dissolves to some extent in water and glacial acetic acid on heating, but the greater part undergoes hydrolysis; it is very slightly soluble in chloroform, but insoluble in light petroleum. It melts at about

245°. Its behaviour is in every way that of a typical nitrogen chloride. When added to strong hydrochloric acid, chlorine is liberated, the halogen escaping rapidly with effervescence ; it liberates bromine from hydrobromic acid, iodine from hydriodic acid ; it oxidises sulphites to sulphates and sets free sulphur from hydrogen sulphide, cyanuric acid in all cases being reformed. When added to ammonia a violent action which may become explosive takes place, nitrogen is evolved, and cyanuric acid reformed. When boiled with water, dilute acids or alkaline hydroxides, it is hydrolysed, cyanuric acid and hypochlorites or the products of their transformation chlorides and chlorates, being produced.

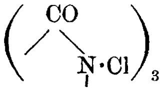
The percentage of chlorine was estimated by Carius' method, and several of the reactions referred to above have been quantitatively studied:

0·3280 gave 0·6052 AgCl. $Cl = 45{\cdot}62$.

$O_3C_3N_3Cl_3$ requires $Cl = 45{\cdot}75$ per cent.

A weighed quantity was added to a solution of potassium iodide, made acid with acetic acid, and the iodine liberated estimated by thiosulphate:

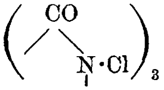
0·4177 liberated $I = 107{\cdot}9$ c.c. *N*/10 iodine. Cl as $:N{\cdot}Cl = 45{\cdot}78$.



requires 45·75 per cent.

A weighed quantity was dissolved in acetic acid, an excess of an approximately decinormal solution of sodium sulphite was added, and the excess afterwards estimated by a standard solution of iodine.

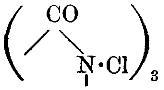
0·2783 oxidised 71·9 c.c. *N*/10 $Na_2SO_3/2$. Cl as $:N{\cdot}Cl = 45{\cdot}79$.



requires 45·75 per cent.

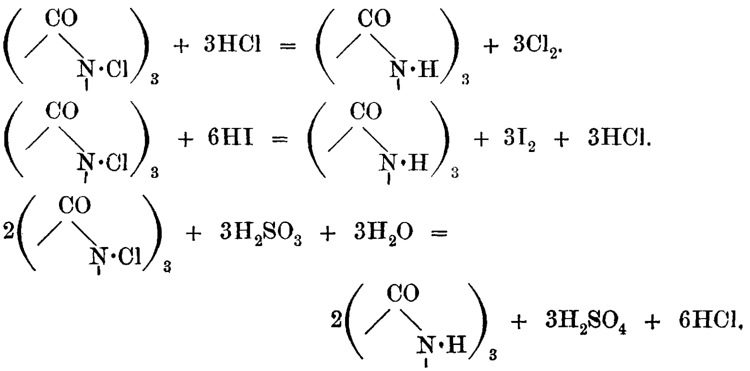
A weighed quantity was heated with an excess of strong hydrochloric acid, in a current of carbon dioxide, in an apparatus with ground glass joints (*Chem. News*, 1899, 85) and the evolved chlorine passed into a solution of potassium iodide.

0·4689 evolved $Cl = 120{\cdot}9$ c.c. *N*/10 iodine. Cl as $:N{\cdot}Cl = 45{\cdot}7$.



requires 45·75 per cent.

These actions are represented by the equations:



The reaction with hydrogen sulphide cannot be used to estimate the amount of chlorine attached to nitrogen, as this substance, like all nitrogen chlorides, oxidises a variable amount of the liberated sulphur to sulphuric acid.

Action of Bromine on Potassium Cyanurate.

When bromine is added to a solution of cyanuric acid in the theoretical amount of a 5 per cent. solution of caustic potash, a pale yellow substance separates from the liquid. This on exposure to air rapidly decomposes, bromine being evolved; it cannot therefore be freed from water and analysed. It liberates iodine from hydriodic acid and violently decomposes ammonia with evolution of nitrogen, cyanuric acid being reformed in each case. When dried over sulphuric acid in an atmosphere of bromine, a pale orange-coloured powder is obtained which gives off bromine slowly at the ordinary temperature, rapidly at 100°, leaving an orange powder having properties similar to those of the original substance. We have not yet been able to obtain a product which we could regard as a pure substance, the composition varying considerably with slight differences of procedure. A very large number of analyses of different specimens seems to show that the body first formed is a bromine additive product of a bromimino-derivative of cyanuric acid, in which, however, all the imino-hydrogen of the cyanuric acid is not replaced.

Action of Chlorine and Bromine on Potassium Cyanate.

Attempts to prepare a chlorimino-derivative of cyanic acid have hitherto been unsuccessful. When chlorine is passed into a cold solution of potassium cyanate, it is absorbed, gas is evolved, and a white, crystalline powder separates, a very pungent odour, somewhat resembling that of cyanogen chloride, being noticed during the reaction.

The white solid thus obtained is, however, cyanuric acid containing a little (5 to 6 per cent.) trichloriminocyanuric acid; on treating with hydrochloric acid or ammonia to decompose the latter and recrystallising from water, pure cyanuric acid is obtained.

The action of bromine on a solution of potassium cyanate is similar and results in the production either of cyanuric acid or of the product already described as resulting from the action of bromine on a solution of potassium cyanurate. If bromine be added to a 25 per cent. solution of potassium cyanate, rapid evolution of nitrogen and carbon dioxide (approximately in the proportion $N_2 : 2CO_2$) takes place, and the temperature rises to about 80°, if the addition be continued until an excess has been added and this be then removed by boiling; cyanuric acid crystallises out on cooling. If the solution of cyanate be cooled in a freezing mixture and the bromine be added cautiously, similar effervescence takes place and a yellow solid separates which in its composition and reactions resembles closely that obtained by the action of bromine on potassium cyanurate; for example, it liberates iodine from hydriodic acid and nitrogen from ammonia, cyanuric acid being in each case produced.

We are at present engaged in a study of various other reactions of the cyanogen halogen derivatives which appears likely to throw additional light on their structure.

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