CXCVI.—*The Action of Halogens on Silver Salts and on Potassium Cyanate in Presence of Water, with a Note on the Decomposition of Cyanic Acid in Aqueous Solution.*

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Some time ago it was noticed that when iodine and silver cyanate were mixed with water, interaction occurred with the formation of silver iodide. The only soluble product appeared to be carbamide.

This seemed sufficiently interesting to warrant further investigation, as the formation of carbamide was scarcely to be expected from such a reaction, whilst examination of the literature threw no light on the subject. The only researches of a systematic nature on the action of halogens on silver salts seem to be those of Birnbaum and collaborators (*Annalen*, 1869, **152**, 111; also Berl, *Ber.*, 1880, **13**, 1270; 1882, **15**, 456), but in these researches it is mainly the action of dry iodine on dry silver salts of organic acids that has been studied.

For convenience the present communication has been confined to reactions in the presence of water, since it was found that the reactions occurred in wholly different ways according to whether water was present or not.

Reactions in Presence of Water.

It was shown by Jakowkin (*Zeitsch. physikal. Chem.*, 1899, **29**, 656) that chlorine is considerably hydrolysed in aqueous solution, according to the equation:

$$Cl_2 + H_2O = H^{\cdot} + Cl' + HClO.$$

Hydrolysis of a similar type has been shown to occur with bromine solutions (Jakowkin, *ibid.*, 1912, **70**, 188; Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932; Bray and Connolly, *ibid.*, 1911, **33**, 1485). Bray has shown from his own results and those of Sammet (*Zeitsch. physikal. Chem.*, 1905, **53**, 687) that in aqueous iodine solution both of the following reactions occur to an appreciable extent:

$$(1)\quad I_2 + H_2O = H^{\cdot} + I' + HIO.$$
$$(2)\quad 3I_2 + 3H_2O = 6H^{\cdot} + 5I' + IO'_3.$$

The concentrations of the substances present in saturated aqueous solutions of the halogens at 25° are as follows (gram-molecules per litre):

Cl_2 = about 0·13 Cl' = about 0·036
$Br_2 = 0·21$ $Br' = 0·37 \times 10^{-3}$ $HBrO = 1·71 \times 10^{-3}$
$I = 0·00132$ I' = less than $4·0 \times 10^{-5}$ HIO = less than $4·0 \times 10^{-6}$

The IO'_3 concentration, when the solution has attained equilibrium according to the second equation given above, is $0·53 \times 10^{-5}$. Solubility data (Landolt-Börnstein, "Tabellen," 1905) show that the solubility products at 20° for silver halides are:

$$(Ag^{\cdot})(Cl) = 1 \times 10^{-10}, \qquad (Ag^{\cdot})(Br) = 2·5 \times 10^{-14},$$
$$(Ag^{\cdot})(I) = 2 \times 10^{-16}.$$

Even with chlorine, therefore, it is only necessary that the silver ion concentration should reach 3×10^{-9} for interaction to occur with precipitation of silver chloride. The only compound with which we experimented in which the concentration probably does not reach this value was silver acetylide. Silver thiocyanate was the least soluble salt of an ordinary type, and it has a solubility at 20° of $8·3 \times 10^{-7}$ gram-equivalents per litre (Böttger, *Zeitsch. physikal. Chem.*, 1903, **46**, 602).

EXPERIMENTAL.

Silver Acetate and Iodine.—When a solution of silver acetate is treated with iodine, a reaction takes place immediately. If the amounts taken are in the ratio of one atom of iodine to one molecule of silver acetate, the products are silver iodide, silver iodate, and acetic acid. Birnbaum (*loc. cit.*) found that the reaction occurred according to the equation:

$$(3)\quad 6C_2H_3O_2Ag + 3H_2O + 3I_2 = 5AgI + AgIO_3 + 6C_2H_4O_2.$$

We arrived at the same conclusion before finding a reference to Birnbaum's paper. We found, further, that the reaction was accurately quantitative if the silver acetate and iodine are heated with water.

If excess of iodine was added, silver iodate was no longer found in the precipitate, but the filtrate contained iodic acid in addition to acetic acid. This reaction is represented by the equation:

$$(4)\ 5C_2H_3O_2Ag + 3H_2O + 3I_2 = 5AgI + 5C_2H_4O_2 + HIO_3.$$

On the assumption that the reaction occurs between the highly ionised silver acetate and the hydrolysis products of iodine, a simple representation of these reactions is obtained. Reaction 4 then becomes:

$$5Ag^{\cdot} + 5(C_2H_3O_2)' + 3H^{\cdot} + 2I' + IO'_3 = 5AgI + 5C_2H_4O_2 + H^{\cdot} + IO'_3,$$

whilst addition of an additional equivalent of silver acetate (Reaction 3) leads to the precipitation of silver iodate:

$$H^{\cdot} + IO'_3 + Ag^{\cdot} + (C_2H_3O_2)' = AgIO_3 + C_2H_4O_2.$$

It cannot, however, be definitely stated that this is the actual course of the reaction. A satisfactory representation is also obtained by assuming that the first reaction is that given by equation 3, and that the silver iodate then reacts with more iodine according to the equation (Naquet, *Jahresber.*, 1860, 201):

$$5AgIO_3 + 3H_2O + 3I_2 = 5AgI + 6HIO_3.$$

Silver Sulphate and Bromine.—Water was added to a weighed amount of silver sulphate, and bromine was aspirated through this mixture until the water remained permanently coloured with the bromine. The precipitate formed consisted of silver bromide, and the solution contained sulphuric acid and either hypobromous or bromic acid, according to the temperature at which the experiment was conducted. The main reaction, if the solution was kept near 0°, led to the formation of hypobromous acid, according to the equation:

$$Ag_2SO_4 + 2Br_2 + 2H_2O = 2AgBr + 2H_2SO_4 + 2HBrO.$$

If the solution was heated, bromic acid was obtained instead of hypobromous acid:

$$5Ag_2SO_4 + 6Br_2 + 6H_2O = 10AgBr + 5H_2SO_4 + 2HBrO_3.$$

The weight of silver bromide obtained was slightly lower than that calculated, possibly because some of the silver sulphate particles became coated with silver bromide, and thus prevented further action. Dancer (*Journ. Chem. Soc.*, 1862, **15**, 477) utilised the similar action of bromine on silver nitrate as a mode of preparing hypobromous acid.

It was mentioned in the introduction that iodine in aqueous solution is hydrolysed in two ways, and in pure water yields both hypoiodous acid and iodate ions. Reactions with iodine therefore usually result in the formation of an iodate. With chlorine and bromine solutions there appears to be little, if any, tendency to form chlorate and bromate by hydrolysis at the ordinary temperature, and reactions with chlorine and bromine therefore yield hypochlorous or hypobromous acids. The formation of bromic acid when bromine and silver sulphate react in hot solution may be due to appreciable hydrolysis of bromine according to the equation:

$$3Br_2 + 3H_2O = 6H^{\cdot} + 5Br' + BrO'_3.$$

It may, however, be equally well accounted for by secondary decomposition of hypobromous acid:

$$3HBrO = 3H^{\cdot} + 2Br' + BrO'_3.$$

When the current of bromine was stopped before all the silver sulphate was decomposed, the solution, after being filtered from silver bromide and bromate, possessed certain properties which indicated the presence of a small amount of a hypobromite and of a silver salt. It seemed possible that the silver salt was silver hypobromite, but as the alleged existence of this salt rests on some rather inconclusive experiments of Balard (*J. pr. Chem.*, 1835, **4**, 179), attempts were made to prepare it from silver oxide and bromine, according to Balard's method.

Silver Oxide and Bromine.

Non-existence of Silver Hypobromite.—Silver oxide, which had been freshly precipitated and well washed, was added to water, and bromine vapour was aspirated through the mixture, which was kept cold by being surrounded by ice. The bromine was immediately decolorised, and silver bromide formed. The action was always stopped before all the silver oxide was decomposed. After filtering, the precipitate was found to be a mixture of the bromide, bromate, and oxide of silver. The presence of silver bromate was proved by shaking the precipitate with a potassium bromide solution and then acidifying. The liberation of bromine showed that bromate was present.

The filtrate had an odour similar to that of bleaching solution, and it decolorised indigo. On account of this oxidising action, it was not possible to determine by means of the ordinary indicators if the solution was acid. Without being acidified, however, it liberated iodine from a solution of potassium iodide, which would indicate that some hydrion was present in addition to an oxidising radicle. It is probable that the acidic substance was hypobromous acid.

When a solution of potassium bromide was added, a precipitate of silver bromide was obtained. This proved that the solution contained silver, but no bromide. The amount of silver bromide so obtained from 100 c.c. of solution was 0·10 gram, which is a little less than would be obtained from a saturated solution of silver bromate at the ordinary temperature.

The solution slowly deposited silver bromide, a decomposition which was accelerated by boiling. From 100 c.c. of a solution, which had been kept for a fortnight and then heated for some time on the steam-bath, 0·03 gram was deposited. This slow production of silver bromide was probably due to slow decomposition of the hypobromous acid into bromic and hydrobromic acids, with subsequent interaction between the silver bromate and hydrobromic acid.

There is therefore no evidence of the existence of silver hypobromite, even in solution. Bromine water appears to react with silver oxide just as it does with mercuric oxide. In both cases the bromide ions formed by the hydrolysis

$$Br_2 + H_2O = H^{\cdot} + Br' + HBrO$$

are removed from the solution by formation of insoluble or non-ionised bromide, and the reaction therefore continues with formation of hypobromous acid.

Silver Cyanate and Iodine.—The silver cyanate was prepared from silver nitrate and carbamide as described by Walker and Hambly (Trans., 1895, **67**, 746). It had been carefully dried and proved by analysis to be pure, although it darkened slightly on long exposure to light. Silver cyanate and iodine in presence of water reacted very slowly in the cold, but more quickly on boiling. The mixture evolved carbon dioxide steadily, and the characteristic odour of cyanic acid was noticeable. The reaction proceeded much faster when the solution was warmed, but the black colour of the iodine did not entirely disappear until the mixture had been heated for several hours on the steam-bath. From analogy to the reactions already described, the action which may be expected is that shown by the equation:

$$6AgCNO + 6I + 3H_2O = 5AgI + AgIO_3 + 6HCNO.$$

The insoluble residue was found to be silver iodide and iodate in agreement with this equation. The solution was at first strongly acid, but became neutral. On evaporation, a white, crystalline solid was obtained, which was found by qualitative analysis to be mainly carbamide, with traces of an organic silver salt and an iodine compound. Several recrystallisations from alcohol were necessary before the carbamide was obtained in a pure form. During the first evaporation to dryness a volatile substance with an extremely unpleasant odour was given off. The crystals obtained by the first crystallisation from alcohol blackened quickly in the light, although too little silver was present to yield even an opalescence with potassium iodide. The impurity after it had blackened was insoluble in alcohol, and could therefore be separated, but it was only entirely removed after four crystallisations from alcohol, although the amount present was extremely small. After four crystallisations from alcohol, the melting point was 131—132°, identical with that of a sample of pure carbamide in the same apparatus. It was identified by the biuret and other well-known reactions for carbamide. The nitrogen was estimated by Kjeldahl's method. (Found, N=46·6. Calc., N=46·7 per cent.)

The acid reaction and the odour of cyanic acid indicate that the first stage of this reaction is that indicated by the equation given above. Cyanic acid is unstable, and yields carbamide on boiling with water, so that the complete reaction may be represented by the equation already given, followed by the conversion of the cyanic acid into carbamide:

$$2HCNO + H_2O = CO(NH_2)_2 + CO_2.$$

In an experiment in which 30 grams of silver cyanate and 25 grams of iodine were boiled with water, the weight of carbamide after one crystallisation from alcohol was 4·1 grams. The yield of carbamide to correspond with the above equations would be 5·9 grams, so that there is no doubt that these equations represent the main reaction. There was some loss of cyanic acid as vapour, as was evidenced by the odour. No other substances were obtained in sufficient amount to be identified.

Note on the Decomposition of Cyanic Acid by Water.

The above representation of the reaction between silver cyanate, iodine, and water afforded a simple and satisfactory explanation of the experimental phenomena, but it appeared at first sight to be irreconcilable with certain statements in the literature as to the decomposition of cyanic acid by water. The main facts in regard to this action are briefly as follows:

(1) Cyanic acid, when liberated from a concentrated solution of potassium cyanate by cautious addition of acetic acid, yields, as the main product, potassium hydrogen cyanurate. The reaction is therefore similar to the polymerisation of anhydrous cyanic acid, and may be represented by the equation:

$$3HCNO = (HCNO)_3.$$

We would suggest that this is the typical mode of decomposition of non-ionised cyanic acid, and that formation of cyanuric acid will occur whenever non-ionised cyanic acid is present.

(2) It has been found (Cumming, Trans., 1903, **83**, 1391) that lead cyanate is decomposed by water with formation of lead carbonate and carbamide, the complete reaction being expressed by the equation:

$$Pb(CNO)_2 + 2H_2O = PbCO_2 + CO(NH_2)_2.$$

O. and I. Masson (*Zeitsch. physikal. Chem.*, 1910, **70**, 290) have found that the reaction is a general one for all metallic cyanates, and that the reaction takes place in two stages:

$$(1)\ CNO' + 2H_2O \longrightarrow NH_4CO_3' \rightleftharpoons NH_4^{\cdot} + CO_3''$$
$$(2)\ CNO' + NH_4^{\cdot} \longrightarrow CO(NH_2)_2.$$

The primary unimolecular reaction between the cyanate ions and water was found to be much slower than the secondary bimolecular reaction between the cyanate and ammonium ions (Walker and Hambly, *loc. cit.*). The experimental results of O. and I. Masson agree well with this hypothesis as to the course of the reaction with various metallic cyanates. The decomposition of cyanic acid differs, however, from that of a salt, such as barium cyanate, in that account must be taken of the effect of the hydrion concentration. With barium cyanate, the hydrion concentration probably becomes constant as soon as a precipitate of barium carbonate appears, and the hydrion therefore functions simply as a catalyst.

(3) Cyanic acid, when liberated from a cyanate by addition of a mineral acid, is decomposed with formation of an ammonium salt and carbon dioxide. With excess of a mineral acid, the whole of the cyanate is decomposed in this manner (Cumming and Masson, *Proc. Soc. Chem. Ind. Victoria*, 1903, 26 and 56). The complete reaction may be represented by the equation:

$$2H^{\cdot} + CNO' + H_2O = NH_4^{\cdot} + CO_2.$$

(4) With a pure cyanic acid solution, we should expect that each of the above reactions will play some part. In the first place, it may be pointed out that the neutral reaction of the alkali cyanates indicates that cyanic acid is a strong acid, and that it will therefore be highly ionised in dilute solution.

In dilute solution therefore the reaction

$$2H^{\cdot} + 2CNO' + H_2O = NH_4^{\cdot} + CNO' + CO_2$$

should occur. Since the hydrion disappears at twice the rate of the cyanate ion, this reaction will be complete when half the cyanate has been decomposed. The remaining cyanate ions should react with the ammonium ions with production of carbamide.

Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, [ii], **20**, 369) found that cyanic acid reacted with water to yield ammonium hydrogen carbonate, whilst at the same time some carbamide and cyamelide were formed. Our experiments with silver cyanate and iodine had suggested that the main product of the decomposition of cyanic acid by water was carbamide, and some further experiments were therefore performed.

A solution of cyanic acid was prepared by mixing a measured volume of *N*-hydrochloric acid with slightly more than an equivalent amount of silver cyanate. The solution, after about an hour, became alkaline in reaction, and, on warming, evolved a little ammonia. Carbon dioxide was also given off, but there was no vigorous effervescence as described by Liebig and Wöhler, a difference due perhaps to the use of a less concentrated solution. After filtration, the precipitate was examined; it appeared to be silver chloride and cyanate only, with no cyanuric acid. The filtrate was evaporated to dryness, and yielded crude carbamide (melting at about 118°). In two experiments the yield of crude carbamide was determined.

Hydrochloric acid, c.c. of *N*-solution.	Weight of AgCNO added, grams.	Crude carbamide obtained, grams.	Calculated possible yield, grams.
100	16	2·8	3·0
280	45	7·0	8·4

During the evaporation to dryness there was a steady loss of carbon dioxide and ammonia, and a few milligrams of a white, insoluble residue separated before the carbamide began to crystallise. The insoluble residue, from qualitative tests, appeared to be cyanuric acid, and its separation was doubtless due to hydrolysis of ammonium cyanurate with loss of the ammonia during the evaporation. The residue was dissolved in alcohol, and filtered from the small amount of insoluble cyanuric acid. The filtrate, on evaporation to dryness, was found to be pure carbamide.

In *N*-solution therefore the main product of the decomposition of cyanic acid is carbamide, with a smaller amount of ammonium hydrogen carbonate and a trace of ammonium cyanurate.

The three modes of decomposition of aqueous cyanic acid may be expressed by the equations:

I. $3HCNO = (HCNO)_3$.

II. $CNO' + H_2O + 2H^{\cdot} = 2NH_4^{\cdot} + CO_2$.

III. $2H^{\cdot} + 2CNO' + H_2O = CO(NH_2)_2 + CO_2$.

The first equation gives the method of decomposition of non-ionised cyanic acid, and indicates the main reaction in concentrated solution. The second equation shows the action of acid on any cyanate, whilst the third equation indicates the main reaction in dilute solution when no other acid is present.

Silver Cyanate and Bromine.—When bromine water was added to silver cyanate there was a very vigorous reaction. In one experiment, when some liquid bromine was poured in with the bromine water, most of the mixture was driven out of the flask by the gas liberated. The gas was found to be a mixture of carbon dioxide and nitrogen. The insoluble residue was silver bromide, and contained no cyanuric acid. The filtrate, which was acid in reaction, was found to contain ammonium bromide, and, in somewhat smaller amounts, carbamide and ammonium cyanurate. Some hypobromous acid was also present.

The formation of nitrogen is probably due to secondary interaction between carbamide and hypobromous acid. With 50 grams of silver cyanate and a slight excess of bromine water (concentration not detérmined, but the solution was saturated at room temperature), about 100 c.c. of nitrogen was obtained. In this experiment the filtrate, on evaporation to dryness, yielded 9·8 grams of a deliquescent mixture, of which the main constituents were ammonium bromide, carbamide, and cyanuric acid.

The reaction appears therefore to resemble the reaction between silver cyanate and iodine, but is faster on account of the greater solubility and larger hydrolysis of the bromine. The secondary reactions are also much more marked, in agreement with the greater oxidising power of hypobromous as compared with iodic acid.

Silver Thiocyanate and Iodine.—When silver thiocyanate and iodine were shaken with water, there was an immediate production of silver iodide. If this action were analogous to that with silver acetate, then the products to be expected would be silver iodide, silver iodate, and thiocyanic acid, provided the silver thiocyanate were taken in excess.

Silver iodate, however, was not formed. The solution was found to contain sulphuric acid, hydrocyanic acid, ammonia, and carbon dioxide in addition to thiocyanic acid.

Some quantitative estimations of this reaction were made, in each case the silver thiocyanate being taken in excess of the amount calculated for the interaction of a molecule of silver thiocyanate and an atom of iodine.

In one experiment 3·967 grams of silver thiocyanate and 2·819 grams of iodine were mixed with water, and the whole was boiled and filtered. The precipitate, after being washed and dried, weighed 5·466 grams. Calculating on the supposition that all the iodine went to form silver iodide, one expected 5·218 grams of silver iodide and 0·269 gram of silver thiocyanate, a total weight of 5·487 grams. This agreement was satisfactory, since some iodine escaped as vapour on boiling the mixture.

In the following experiments the filtrate was made up to a known volume. The thiocyanic acid was estimated volumetrically by titration with standard silver nitrate, and the cyanide determined in another portion by Volhard's method, excess of sodium hydroxide and a drop of potassium iodide solution being first added. The presence of iodide ions is here necessary. Otherwise the soluble complex salt, $KAg(CNS)_2$, is also formed, and the true end-point of the formation of $KAg(CN)_2$ is not obtained. The ammonia was determined by boiling with excess of sodium hydroxide and titration of the distillate. The sulphuric acid was determined gravimetrically by precipitation with barium chloride.

Expt. I was carried out in the cold, the mixture being well shaken.

Expt. II. The mixture was boiled (when hydrogen cyanide must have escaped).

Expt. III. The mixture was boiled, and the distillate was received in standard sodium hydroxide. Nearly all the hydrogen cyanide distilled over, in addition to carbon dioxide.

The results are as follows, the numbers being given in gram-molecules, except in the case of iodine, which is given in gram-equivalents:

	I.		II.		III.	
Reacting substances.	Found.	Calc.	Found.	Calc.	Found.	Calc.
AgCNS ...	0·0398	—	0·0294	—	0·0313	—
I	0·0391	0·0322	0·0273	0·0262	0·0293	0·0289
Reaction products.						
HCNS......	0·0276	0·0276	0·0225	0·0225	0·0248	0·0248
HCN	0·0025	0·0023	[0·0007]	0·0019	0·0024	0·0021
H_2SO_4......	0·0047	0·0046	0·0037	0·0037	0·0042	0·0041
NH_3	(not estimated)	0·0023	0·0029	0·0019	0·0025	0·0021

The calculated values given in the table were obtained from the equation:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2,$$

the basis of calculation being the amount of thiocyanic acid produced. The calculations were not made from the amount of iodine originally weighed out, because some iodine escaped as vapour when the solutions were heated, and, when cold, the particules of iodine seemed to become coated with silver iodide.

Accordingly, the table shows the calculated values for iodine to be less than the experimental. Otherwise the agreement of the experimental with the calculated values is satisfactory. Unlike the reactions described above, this reaction results in the oxidation of part of the thiocyanic acid. The formation of the products actually obtained necessitates the supposition that two oxidations are proceeding simultaneously, namely:

$$HCNS + H_2O + 3O = HCN + H_2SO_4,$$
$$\text{and } HCNS + 2H_2O + 4O = H_2SO_4 + NH_3 + CO_2.$$

The equation for the whole reaction corresponding with these oxidations are respectively:

$$6AgCNS + 3I_2 + 4H_2O = 6AgI + 5HCNS + HCN + H_2SO_4,$$

and

$$8AgCNS + 4I_2 + 6H_2O = 8AgI + 7HCNS + H_2SO_4 + NH_3 + CO_2.$$

It follows that the actual reaction must have proceeded equally in each of these directions, since by the addition of these two equations there is obtained the equation with which the experimental results agree, namely:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 14HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2.$$

Silver Sulphite and Iodine.—From the experiments with silver thiocyanate and iodine it appeared probable that, whenever the primary reaction led to the formation of an oxidisable acid, an oxidation product would be obtained. In accord with expectations, it was found that silver sulphite and iodine yielded only silver iodide and sulphuric acid, even when the silver sulphite was taken in excess:

$$Ag_2SO_3 + I_2 + H_2O = 2AgI + H_2SO_4.$$

Silver Thiocyanate and Chlorine.—Silver chloride is more soluble than the thiocyanate, the solubilities at 20° being: AgCNS, $8{\cdot}27 \times 10^{-7}$ gram-molecules per litre, and AgCl, $1{\cdot}06 \times 10^{-5}$ gram-molecules per litre. In the introduction it was suggested as a working hypothesis that the interaction of a silver salt and a halogen depends on the hydrolysis of the halogen in aqueous solution. Any silver salt with an ionic concentration above 3×10^{-9} should, if this hypothesis is correct, react with a saturated chlorine solution. In spite of its lower solubility therefore, silver thiocyanate should yield silver chloride on treatment with a saturated chlorine solution.

It was found that interaction occurred at the ordinary temperature, but that the action did not proceed to completion. (The action should stop when the chlorine concentration has fallen to a certain value even if some silver thiocyanate be present. This point was only tested qualitatively.) The products of the reaction were: silver chloride; sulphuric, hydrocyanic, and hydrochloric acids; and ammonia.

Potassium Cyanate and Bromine.—As the potassium cyanate used in these experiments contained some carbonate, it was analysed, the carbonate being precipitated as barium carbonate, and the cyanate as silver cyanate. These analyses gave the factor for actual potassium cyanate present as 0·929, and for carbon dioxide as 0·0420. Bromine water acted immediately at the ordinary temperature on a solution of potassium cyanate. A gas containing carbon dioxide and nitrogen was evolved, and an examination of the liquid after the excess of bromine was boiled off proved the presence of potassium and ammonium bromide.

In a series of quantitative experiments excess of bromine was added to a solution containing a known amount of potassium cyanate. The solution was then boiled under a reflux condenser until it became colourless. The gas evolved was led through a series of tubes containing (1) sulphuric acid, (2) phosphoric oxide, (3) red phosphorus, which had been dried in a vacuum desiccator and which retained the excess of bromine, (4) and (5) soda-lime.

The carbon dioxide produced was determined from the weights of the soda-lime tubes before and after the experiments.

The solution was made up to a known volume, and from portions of this, both bromide and ammonium were volumetrically determined.

The results, given in gram-equivalents, were as follows:

	Substance, gram.	CO_2.		Br.		NH_3.	
		Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	0·6905	[0·00952]	0·00827	0·01290	0·01260	0·00279	0·00395
2.	0·6234	0·00770	0·00747	0·01185	0·01138	0·0025	0·00357
3.	0·6674	0·00785	0·00800	0·01170	0·01218	0·00273	0·00383

In experiment (1) the red phosphorus had not been properly dried, so that hydrogen bromide passed over into the soda-lime tubes, and probably caused the carbon dioxide result to be too high. In order to estimate the nitrogen liberated, a solution containing a known amount of potassium cyanate was placed in a flask closed by a rubber cork, through which there was fitted a long glass tube which served as a condenser and was closed at the top by a glass tap. The flask and tube were exhausted by means of a Töpler air-pump. Excess of bromine was allowed to enter the flask by means of the tube, and the solution was then boiled, the stop-cock being closed. The flask was again exhausted, the gas evolved being led through a tube of soda-lime and fused calcium chloride to remove the water vapour, carbon dioxide, and bromine. The nitrogen was collected in a measuring tube over mercury, and was measured at atmospheric pressure.

The ammonium salt in solution in the flask was also estimated.

The experimental results are given below in gram-equivalents.

In experiment *A* there were taken 50 c.c. of a solution containing 0·7568 gram of the impure potassium cyanate dissolved in 250 c.c. of water. In each of the experiments *B* there were taken 25 c.c. of a solution containing 3·045 grams dissolved in 500 c.c. of water:

		KCNO corrected.	Nitrogen obtained as gas.	NH_3 in solution.	Total N obtained.
A	...	0·00868	0·00488	0·00397	0·00885
B.	1.	0·0349	0·0193	0·0165	0·0358
	2.	0·0349	0·0207	0·0135	0·0342
	3.	0·0349	0·0186	0·0168	0·0354

The calculated values given in the tables have been obtained from the equation:

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

The results show that the main reaction is according to this equation. The amounts of ammonia, however, are consistently lower, and those of nitrogen higher, than their calculated values, although the total nitrogen is well accounted for. Possibly this is due to a side reaction, namely, the action of a hypobromite on carbamide. The carbamide could be formed from ammonium and cyanate ions, which must be in solution together during the progress of the reaction, and hypobromite would be formed by the action of bromine on the carbonate originally present with the cyanate.

Silver Acetylide and Iodine.—The action of iodine on silver acetylide in presence of water was found to be quite unlike the reactions described above. Reaction occurred very slowly, and it was found that for each atom of silver present at least two atoms of iodine were required. The insoluble residue appeared to be a mixture of silver iodide and acetylide. The filtrate was extracted with ether, and on evaporating the ether a very small residue, the vapour of which attacked the eyes and possessed an extremely unpleasant odour, was obtained.

It is probable that this residue contained the substance $C_4H_2I_4$, crystals of which Berend (*Annalen*, 1865, **135**, 258) obtained by the action of an ethereal solution of iodine on silver acetylide.

Silver Acetate and Cyanogen Iodide.—This reaction was examined in the hope that silver iodide would be formed, together with some product of the interaction of the cyanogen and acetate radicles, but this did not take place.

The cyanogen iodide was prepared by subliming the precipitate obtained by the addition of iodine to a solution of potassium cyanide.

Quantities in the ratio of a molecule of cyanogen iodide to a molecule of silver acetate were weighed out and dissolved in water. A white precipitate was slowly formed, but even after four days this precipitation was not complete. The precipitation was slightly accelerated by boiling the solution, but on continuing the evaporation to dryness a considerable amount of silver acetate was found to be still undecomposed. During this evaporation the cyanogen iodide must have been lost, for when the solution was boiled under a reflux condenser, solid cyanogen iodide was found to condense within the condenser. The precipitate obtained in this reaction was a mixture of silver cyanide, iodide, and iodate.

The action of cyanogen iodide therefore on silver acetate appears to be similar to that of iodine, but the slowness of the reaction is probably due to the excessively small number of ions it forms in water. It may be noted that when a solution of potassium hydroxide was added to the original solution, a copious precipitate of silver iodide immediately appeared.

Summary.

The halogens react with silver salts to yield an insoluble silver halide, an acid, and one or more oxidation products of either the acid or the halide. A simple, typical case is the action of iodine on silver acetate, which is represented by the equation:

$$3I_2 + 3H_2O + 5C_2H_3O_2Ag = 5AgI + HIO_3 + 5C_2H_4O_2.$$

The reactions, on account of secondary oxidations, are sometimes complex; for example, silver thiocyanate and iodine interact according to the equation:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2.$$

The oxidation reactions were much more marked with chlorine and bromine than with iodine, on account probably of the greater oxidising power of hypochlorous and hypobromous acids as compared with iodic or hypoiodous acids.

The main product obtained by treatment of silver cyanate by iodine was carbamide, formed probably by secondary decomposition of cyanic acid. Bromine and silver cyanate yield ammonium bromide, carbamide, cyanuric acid, and a little nitrogen.

For comparison the interaction of bromine and potassium cyanate was studied, and found to be in accord with the equation:

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

It is suggested that the reactions are due to interactions with the products of the hydrolysis of the halogen by water; thus, a silver salt reacts with the halide ions formed by partial hydrolysis of the halogen, for example:

$$Cl_2 + H_2O = H^{\cdot} + Cl' + HClO.$$

Further interaction may occur between the hypochlorous acid and one of the other reaction products.

The experimental results are in accord with this hypothesis.

In connexion with the formation of carbamide, some experiments on the decomposition of aqueous cyanic acid were tried, and these, in conjunction with previous work, led to the conclusion that cyanic acid decomposes in three different ways according to the conditions of experiment. In concentrated solution the main reaction is the formation of cyanuric acid, probably by polymerisation of non-ionised cyanic acid molecules. Acids decompose cyanic acid according to the equation:

$$CNO' + H_2O + 2H^{\bullet} = 2NH_4^{\bullet} + CO_2.$$

In dilute solution cyanic acid decomposes itself, according to the above equation, until all the hydrion has been used up. The ammonium ions and the remaining cyanate ions interact to form carbamide. The whole reaction is expressed by the equation:

$$2H^{\bullet} + 2CNO' + H_2O = CO(NH_2)_2 + CO_2.$$

In conclusion we desire to take this opportunity of expressing our indebtedness to Prof. James Walker for his valuable advice and criticism throughout the research.

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