CXXXIX.—*The Bromination of Silver Cyanate.*

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DURING some experiments on the preparation of certain cyanogen compounds, equivalent weights of silver cyanate and bromine were taken in a sealed tube and gently heated, the bromine being introduced in a thin glass bulb. On opening the tube, most of the halogen had disappeared, only a trace of vapour remaining in the enclosed air. The solid residue appeared to be an additive compound of silver cyanate and bromine. When heated, it gave off bromine, and on the addition of water decomposed with effervescence, bromine being evolved. Other specimens, which had been freed from uncombined bromine by being kept for several weeks over caustic soda, iron filings, or in a vacuum, behaved similarly.

The substance was of a brittle, friable nature, and had a deep yellow colour quite distinct from that of silver bromide; when exposed to light in a tightly-stoppered bottle, it preserved its colour indefinitely. In the presence of traces of moisture, silver bromide was produced, the colour fading to a pale yellow which slowly blackened. When a tube containing the substance was plunged into a bath of sulphur at 300—400°, the bromine evolved was accompanied by a thick white sublimate of cyanogen bromide. At that temperature, an interaction had evidently taken place between part of the liberated halogen and the silver cyanate.

The following experiment was made in order to find out the reacting proportions. Ten grams of cyanate were placed in a small, stoppered

distilling flask and bromine added until the whole was liquid. During the reaction, the heat evolved was sufficient to produce an appreciable rise in temperature. Next morning, the dark brown mass had solidified, and showed signs of crystalline structure, the surface being crossed by several fine long needles.

The greater portion of the excess of bromine present was drawn off with the aid of the water-pump, but some difficulty was experienced in getting rid of the last traces without having to raise the temperature. On gently heating, a few minute rosettes of needle-shaped crystals were seen to have condensed from the vapour. These crystals, which volatilised during the course of the experiment, probably consisted of cyanogen bromide.

The final weight of the brominated cyanate was 15.065 grams, corresponding with an addition of 76 units per molecule of the silver salt.

The presence of cyanogen bromide in the vapour would be explained if the reaction on bromination had followed the course represented by the equation :

In that case, it should have been accompanied by free oxygen. To determine if this were so, several grams of silver cyanate were treated with bromine in an exhausted flask and the gas pumped out by means of a Sprengel pump. About 80 c.c. were obtained and found on analysis to be a mixture of carbon dioxide and nitrogen, roughly in the proportions 1 to 2.5, but no oxygen was present. The bromine used had not in this instance been specially dried, and I suspected that the gas produced might be due to the oxidising action of the moist halogen, especially as the increase in weight after bromination was much lower than usual. The experiment was accordingly repeated with fresh material, which was prepared as follows. The silver cyanate was obtained by evaporating a solution containing silver nitrate and urea in molecular proportions. The mass of fine needle-shaped crystals which separated was repeatedly washed with hot water, drained, dried in a vacuum, heated for several hours at 100°, and finally left for some weeks over concentrated sulphuric acid in a vacuum. Commercial bromine was well washed with water, and then left with successive solutions of potassium bromide which removed chlorine and cyanogen chloride. Traces of iodine were eliminated by means of zinc oxide, and water was removed by fused zinc bromide. The bromine thus purified was finally distilled from fresh zinc bromide and the first and last portions of the distillate rejected.

On repeating the bromination in a vacuum with the dried substances, several grams of cyanate evolved only 5 c.c. of gas, consisting approximately of 1 vol. of carbon dioxide and 2 of nitrogen. In no instance

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could any appreciable amount of oxygen have been produced, and the gas evolved is apparently due to a secondary reaction caused by the presence of water.

In order to determine the weight of bromine retained by the cyanate when the conditions of temperature and pressure were varied, the apparatus used was modified somewhat; bromination was effected in a Wurtz flask, provided with a well-ground stopper, the side-tube being connected with a large glass bulb, which also had two other outlets. One of these communicated with a water-pump, through a wash-bottle containing strong sulphuric acid, and the other could be quickly opened to the air. The glass bulb thus employed served as a trap between the flask and the drying bottle, and the latter prevented the passage of water vapour from the pump to the substance.

Much heat was evolved on bromination, and the product was then left until the next day, more bromine being added on successive days until the mass was quite liquid. Excess of bromine was then removed by heating the flask to about 60° in a water-bath and gradually diminishing the pressure to 300—400 mm. of mercury. As soon as the space above the solid appeared to be free from bromine vapour, the flask was disconnected and weighed. This gave the first determination of the added bromine. The flask was then replaced, exhausted, and weighed. The details of the separate treatments, together with the results obtained, are given below.

Bromine.

1st exhaustion—continued until no bromine vapour could be seen at 60° under 300—400 mm. pressure. Increase in weight per molecule of cyanate.....	90.56
2nd „ continued for 30 mins. at same temperature and pressure as before.....	82.6
3rd „ continued for 30 mins. at same temperature and pressure as before.....	81.7
4th „ continued for 30 mins. at same temperature and pressure as before.....	81.3
5th „ continued for 30 mins. at same temperature and pressure as before.....	81.0
6th „ after long exhaustion at 100° (300—400 mm.)...	79.74
7th „ after long exhaustion in the cold (300—400 mm.)	79.74
8th „ after long exhaustion to 10—20 mm. in the cold	79.66
9th „ on heating at 100° for 15 mins., bromine was seen to be coming off, and therefore no weighing was made.	
10th „ on heating at the temperature of a saturated calcium chloride solution, bromine was evolved.	

Bromine.

11th exhaustion—on heating at 220° , there was a steady evolution of bromine vapour, which was still being given off when the apparatus was disconnected 66.92

The conclusions drawn from the foregoing experiment are as follows:

1. The weight remains fairly steady when the composition of the product corresponds with the formula $(\text{AgCNOBr})_x$.
2. Dissociation does not take place below 70° , but begins below 100° and is not complete at 200° .
3. At the ordinary temperature, dissociation can be produced by lowering the pressure to 10–20 mm. of mercury.

Action of Different Reagents on the Substance.

Water.—Treatment with water causes an effervescence due to a mixture of gas and bromine vapour. In order to test the gas produced, the substance was introduced into a small flask provided with a dropping funnel and connected with a Sprengel pump by means of a tube packed with iron wire, to absorb the bromine. The flask was exhausted and the gas which was evolved on the addition of water was pumped out and tested; it proved to be a mixture of carbon dioxide and nitrogen in the proportions by volume of 2.5 of the former to 1 of the latter. The solid residue was chiefly silver bromide, but contained in addition a white constituent. To obtain a specimen of this, 10 grams of cyanate were brominated and the product treated with water after removing the excess of halogen. The dry residue weighed 13.6 grams instead of 12.53, as calculated for silver bromide. By careful levigation, a little of the white portion was removed from the bromide and tested. It answered the tests for cyanuric acid, and on combustion the percentages of carbon and hydrogen agreed fairly well with the calculated values. The action of water on the substance is approximately represented by the following equation:

Alcohol.—Absolute alcohol was heated with some of the substance, when a slight evolution of gas took place and a distinct odour of aldehyde was observed. The liquid turned yellow and reduced ammoniacal silver solution. A white deposit settled on the surface of the silver bromide, but was not further examined. The reaction probably took the following course:

Ammonia.—When well-dried ammonia was passed over about 10 grams of the substance enclosed in a tube, white fumes were formed

and a considerable evolution of heat was noticed. The yellow residue, unlike the original substance, then rapidly turned dark, and on further heating gave, in addition to a little ammonium bromide, a white sublimate insoluble in water.

Hydrogen Chloride.—On passing the dried gas over the substance, bromine was at first given off, the amount increasing on gently heating. At the same time, a few drops of clear liquid distilled which gradually turned milky and finally solidified; this product was probably cyanogen chloride, the residue being a mixture of silver chloride and bromide:

A Higher Additive Compound.

Evidence was not wanting of the existence of a more unstable product containing a larger proportion of bromine. In the second experiment, the dark brown solid product had the appearance of such a compound, and as the excess of bromine was removed it lost its superficial crystalline structure. This fact is supported by the following experiments, which were made in order to determine whether bromination at a lower temperature would have any effect on the reacting proportions.

To bring about interaction at a low temperature, bromine vapour was allowed to diffuse gradually in through the silver cyanate. The apparatus used consisted of a small retort, tightly stoppered, to the neck of which a flask was ground. Into the latter, the cyanate was introduced, whilst the bromine was poured into the retort. The progress of the reaction could be traced from the movement of the encroaching ring of additive compound in the mass of cyanate. From time to time, the apparatus was disconnected, the vapour in the flask removed by a current of air, and the increase in weight determined. The rate at which the halogen was taken up diminished gradually, and after about thirty days there was no further addition, the increase then corresponding with 73 parts per molecule of cyanate. After that, the proportion of bromine diminished, a slight decomposition taking place, due probably to the presence of moisture in the aspirated air. The following curve shows the rate of bromination.

Bromine and cyanate from the same samples as those used in the foregoing experiments were next allowed to interact in exactly the same manner, but for a longer period. No disturbance of the apparatus was made for intermediate weighing. On attempting to remove the free vapour from the flask before weighing, by passing air through as before, a copious and prolonged evolution of bromine took place. On weighing the added bromine at this stage, there were still 120 parts

per molecule of cyanate. On again passing air through the flask, more bromine was expelled, and the ordinary yellow product remained.

In order to see whether this additional absorption of bromine could be attributed to any purely mechanical action of the finely-divided compound, an experiment was performed, precisely similar in method, but in which the cyanate was replaced by dry precipitated barium sulphate. No absorption whatever took place, the sulphate remaining

absolutely constant in weight after several months' immersion in the vapour.

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