ON THE CYANOGEN HALIDES

BY P. KAILASAM
(From the Chemistry Department, Madras Christian College)

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I. Action of Halogens on Cyanogen Halides

No observations appear to have been recorded on the action of halogens on cyanogen halides except that of chlorine on cyanogen chloride (Wurtz, 1851; Naumann and Vogt, 1870) and bromine on cyanogen bromide in ether (Poonamarew, 1885) which polymerise them to cyanuric chloride and cyanuric bromide respectively. The object of the present investigation is to study the possible displacement reactions with the cyanogen halides.

The action of chlorine gas on cyanogen iodide and the action of bromine on cyanogen chloride were first studied. It was expected that chlorine would displace iodine from cyanogen iodide forming cyanogen chloride, but it was found that cyanogen iodide was not affected by dry chlorine. Dry cyanogen iodide, prepared by warming an intimate mixture of one part of iodine and two parts of AgCN, at about 40°, was sublimed into a narrow tube which could be heated in a water-bath. Dry chlorine was passed through the tube for nearly two hours. No immediate reaction occurred, and even after leaving for a week at room temperature (30°) the white needles of cyanogen iodide remained unchanged. The tube was then slowly heated, but no reaction occurred up to the sublimation temperature of cyanogen iodide (about 40°). It was found that cyanogen iodide could be sublimed unchanged in an atmosphere of dry chlorine.

Since chlorine does not displace iodine from cyanogen iodide, it was thought that bromine might displace chlorine from cyanogen chloride forming cyanogen bromide. This reaction, however, is not simple.

Experimental

Cyanogen chloride was produced by the action of chlorine on aqueous hydrocyanic acid (10-15%) prepared by distilling potassium ferrocyanide with dilute sulphuric acid. The aqueous HCN was placed in a series of gas washing bottles containing glass beads. The last wash bottle was connected to a U-tube of calcium chloride which was sealed to a glass spiral cooled in...
ice and salt. A steady current of chlorine was then passed through the aqueous hydrocyanic acid. The cyanogen chloride formed condensed in the spiral as a colourless liquid. The liquid CNCI was then purified by passing excess of chlorine to remove any free HCN, treated with pure dry mercury to remove the excess of chlorine, and finally distilled through sodium bicarbonate and calcium chloride to remove HCl and moisture respectively (Price and Green, 1920).

The reaction between bromine and cyanogen chloride was allowed to take place in a U-tube with taps sealed at either end. The bromine was distilled over fused calcium bromide into the apparatus and then the cyanogen chloride was distilled into the same. For about 10 c.c. of liquid bromine, 8-9 c.c. of CNCI were taken. After about 12 hours the liquid mixture of bromine and cyanogen chloride solidified to short needle-shaped crystals. The reaction was allowed to continue for five days more.

After this period, the excess of bromine was removed by passing a current of dry air through the apparatus and then through strong alkali. The alkali was tested in the end and found to contain no cyanogen compound. The solid residue was then treated with pure dry chloroform, in which almost the whole of it dissolved. The solution was filtered and the chloroform distilled off, when a crystalline product was formed. This was re-dissolved in chloroform and crystallised, when shining plates were obtained. Re-crystallisation from petroleum ether (60-80°) gave feather-shaped crystals.

This substance contains Carbon, Nitrogen, Chlorine and Bromine. It melts at 160-61° to a colourless liquid which slowly volatilises as the temperature is raised. It sublimes above 100°. It dissolves in ether, carbon disulphide, carbon tetrachloride, petroleum ether and very readily in chloroform, benzene, and acetone. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but dissolves in hot water. Heated with water at 100-20°, cyanuric acid, HCl and HBr are formed. The substance has a strong, pungent, and irritating odour causing tears in the eyes.

The carbon was estimated by the usual method, and the nitrogen by Dumas method. The total halide was estimated by Piria and Schiff's method, and thence the two halogens were estimated separately by Moser and Miksch method of heating the combined silver halides with pure dry ammonium bromide (to convert the chloride into bromide). On analysis the substance was found to have the composition, Cl = 47.4%, Br = 12.85%, N = 21.43% and C = 18.31%. From the percentage composition, the calculated formula comes to \( \text{C}_9\text{N}_9\text{Cl}_8\text{Br} \) with a molecular weight of 597. But
the molecular weight determined by the cryoscopic method using benzene as the solvent comes to only 206.

0.2298 gm. of substance dissolved in 24.8310 gm. of benzene gave a depression of 0.225° C. (Mol. Weight = 205.6).

0.2477 gm. of substance dissolved in 23.9520 gm. of benzene gave a depression of 0.251° C. (Mol. Weight = 206).

The melting point of substance, however, remains unchanged when crystallised from acetone and carbon tetrachloride and also after subliming.

It is probable the substance is a double compound of two molecules of cyanuric chloride, C₃N₃Cl₃, and one molecule of monobromo cyanuric chloride, C₃N₃Cl₂Br (see below), which dissociates in benzene into two molecules of C₃N₃Cl₃ and one of C₃N₃Cl₂Br. This will explain the observed molecular weight (206) in benzene which is nearly one-third the theoretical (597). It is further proved that the substance is a definite compound from the melting point determinations of mixtures of the two compounds, C₃N₃Cl₃ and C₃N₃Cl₂Br. For, the melting points of mixtures of C₃N₃Cl₃ and C₃N₃Cl₂Br mixed in proportions slightly higher and lower than the theoretical ratio 2:1 were lower than the m.p. (160°) of the substance (C₉N₉Cl₈Br).

m.p. of a mixture of 0.0241 gm. (70.87%) of C₃N₃Cl₃ and 0.0099 gm. (29.13%) of C₃N₃Cl₂Br was 156° C.

m.p. of a mixture of 0.01103 gm. (48.52%) of C₃N₃Cl₃ and 0.0117 gm. (51.48%) of C₃N₃Cl₂Br was 150° C.

Cyanuric chloride is given a cyclic ring structure as 2 • 4 • 6 • trichloro 1 • 3 • 5 • triazin (Chattaway, 1902).

In a similar manner the constitution of C₉N₉Cl₈Br can be expressed either as
The second formula can easily account for the observed dissociation of the compound into three simple molecules in benzene.

**II. Action of Hydrobromic Acid on Cyanuric Chloride**

By the action of aqueous hydriodic acid (57%, constant boiling point acid) on cyanuric chloride in the cold, KIason (1886) observed that besides cyanuric iodide, the compound monochloro cyanuric iodide, $C_3N_3I_2Cl$, was also formed as an intermediate product. This was obtained as white feathery crystals by heating the cyanuric iodide formed at about 360°. So it was expected that by a similar treatment of cyanuric chloride with hydrobromic acid (47% constant boiling point acid) the corresponding bromo compound could be obtained. But instead of the bromo compound $C_3N_3Br_2Cl$, only $C_3N_3Cl_2Br$ was obtained.

**Experimental**

Cyanuric chloride was prepared according to the methods of KIason (1886) and Fries (1886).

Into a flask containing pure dry chloroform, chlorine was passed until saturation. Then chlorine and hydrogen cyanide were both passed simultaneously, keeping the chlorine always in excess and applying strong cooling throughout the experiment. After 12 hours the flask was fitted with a condenser and refluxed until the excess of chlorine, $HCl$ and the unpolymerised $CNCI$ had all escaped. Then the chloroform was distilled off, when a residue of long needle-shaped crystals was got. The product was recrystallised from petroleum ether and dried in a desiccator.

To about a gram of the pulverised cyanuric chloride about 6–8 c.c. of 47% hydrobromic acid were added and constantly stirred. After every three hours, the acid was removed by decantation, fresh acid added and again stirred constantly. The reaction was thus continued for 24 hours. Then it was filtered, washed and dried in a desiccator. The dried product was heated up to 150° when prismatic crystals sublimed. After resubliming it was used for analysis.
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This substance contains Carbon, Nitrogen, Chlorine and Bromine. Most of it sublimes below 200°, only a little melts at 210° which slowly volatilises as the temperature is raised further. It dissolves in all the usual organic solvents. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but when heated with water at 120°, cyanuric acid, HCl and HBr are formed.

On analysis the substance is found to have the composition Cl = 30·4%, Br = 34·31%, and N = 18·22%; C₃N₃Cl₂Br requires Cl = 30·98%, Br = 34·92%, and N = 18·37%.

The m.p. of substance remains unchanged when crystallised from chloroform.

The non-volatile residue left behind on heating the washed and dried product of the reaction of hydrobromic acid on cyanuric chloride, also contained carbon, nitrogen, chlorine and bromine. The quantity of substance available was too small for analysis. It did not melt nor sublime up to 280° C.

Further work is in progress.

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REFERENCES

Naumann and Vogt . . Annalen, 1870, 155, 175.
Klason . . Jour. prk. chem., 1886, 34 (2) 152.
Moser and Miksch . . Page 112, Quantitative Organic Microanalysis of F. Pregl. by Hubert Roth.