XXXIV.—*On a Cyanogen-derivative of Marsh-gas.*

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THE action of cyanide of potassium on chloropicrin appeared, from the other reactions of the latter substance, to promise interesting results. The experiments made in this direction have led to the production of a substance representing chloropicrin in which 2 atoms of chlorine are replaced by cyanogen.

The process adopted was as follows :—

15 grms. of the best fused cyanide of potassium are dissolved in $1\frac{1}{2}$ oz. water, $\frac{3}{4}$ oz. alcohol added, and then 10 grms. chloropicrin.

The flask containing the mixture is fitted with a long condensing tube, and then placed on a water-bath till the reaction is started. It must then be quickly removed, and the upper end of the tube inserted into an opening in the chimney, to avoid inconvenience from the pungent vapours. The liquid rapidly becomes dark red, and a very violent reaction takes place for about ten minutes, sometimes necessitating the cooling of the flask towards the end of that time. The quantities mentioned cannot be safely exceeded, and the proportion of alcohol must not be sufficient to dissolve the chloropicrin, as the action then becomes almost explosive.

The contents of a sufficient number of flasks, when cold, are agitated with ether, and the resulting dark red ethereal solution is separated. The watery liquid remaining is dark brown, from the presence of a considerable quantity of the substances known as azulmic or paracyanic acids, and contains chloride, nitrite, carbonate, and oxalate of potassium, and large quantities of ammonia.

The ethereal solution is heated in a retort in the water-bath, to separate the ether and alcohol as far as possible, and the heat should not be continued too long, the substance being thereby

altered. The residue is mixed with water and filtered from some insoluble matter, the filtrate saturated with chloride of sodium, agitated with ether, separated, and the ethereal solution evaporated in an open vessel at very gentle heat.

The substance thus obtained is semi-fluid, of a dark red colour, does not solidify at -20° , has a peculiar and unpleasant smell, and is soluble in all proportions in water, alcohol, ether, chloroform, &c., the solutions staining the skin bright yellow.

It retains a considerable quantity of water, which is not given up over sulphuric acid in vacuo; neither can it be dried by heat, as even at ordinary temperatures it slowly alters, and near 100° it is completely decomposed. In the solution obtained by boiling it with potash, the presence of chloride, nitrite, and cyanide is readily detected by the usual tests, and large quantities of ammonia are formed.

It was obviously useless to attempt the analysis of this substance, but I think its composition is sufficiently indicated by the analyses of its compounds with oxide of lead and nitrate of silver.

The watery solution was mixed with excess of acetate of lead, filtered from any slight precipitate, and ammonia cautiously added, taking care not to use sufficient to render the liquid alkaline; the bright orange precipitate washed with boiling water and dried at 100° , bears a high temperature without decomposition, and is extremely hygroscopic.

I. .32 grm. gave .3615 grm. $\text{Pb}^{\text{I}}\text{SO}_4$.

II. 1.01 grm. gave .18 grm. AgCl (dissolved in cold dilute nitric acid, nitrate of silver added, and then heated with excess of strong nitric acid till completely decomposed).

III. 3.084 grms. gave .509 grm. CO_2 and .07 grm. H_2O .

IV. .3195 grm. (another preparation) gave .3585 grm. $\text{Pb}^{\text{II}}\text{SO}_4$.

V. .994 grm. gave .184 grm. AgCl .

VI. 1.113 grm. gave 28.3 c. c. N. at 0° and 760 mm.

These results lead to the formula $\text{CNO}_2\text{ClCy}_2 + 3\text{Pb}^{\text{II}}\text{O}$.

	I.	II.	Theory.
Lead	77.19	76.65	76.24
Chlorine	4.41	4.58	4.35
Carbon	4.50	—	4.42
Hydrogen ..	.25	—	—
Nitrogen. . . .	—	3.19	5.16

The percentage of nitrogen is too low, but the fact that the other constituents are all rather in excess of the amounts required, and the impossibility of purifying the substance, will, I think, account for this.

The silver-compound is precipitated as a bulky orange-coloured powder on adding nitrate of silver to the solution of the original substance. It must be washed with cold water, in which it is slightly soluble, and dried in vacuo.

I. ·7287 grm. heated with strong nitric acid till completely decomposed, gave ·248 grm. AgCl, or 8·42 p. c. chlorine.

II. Filtrate from the above, mixed with hydrochloric acid, gave ·0835 grm. AgCl, which, added to the former quantity, gives ·3315 grm. AgCl to represent the whole amount of silver in the substance, or 34·24 p. c.

III. ·4615 grm. decomposed with hydrochloric acid gave ·209 grm. AgCl, or 34·08 p. c. silver.

The formula $3\text{CNO}_2\text{ClCy}_2 + 4\text{AgNO}_3 + 8\text{H}_2\text{O}$ requires 34·27 p. c. silver, and 8·45 p. c. chlorine.

The compound when heated to 80° decomposes suddenly with great frothing, leaving a very bulky residue. The water contained in it may, however, be removed by heating it under boiling water; it then fuses into dark-red drops. A quantity of cold water is then added, and the substance taken out and dried with filter-paper, and afterwards *in vacuo*.

I. ·693 grm., treated with nitric acid as before, gave ·259 grm. AgCl, or 9·25 p. c. chlorine.

II. Filtrate from the above, mixed with hydrochloric acid, gave ·096 grm. AgCl, which, added to the former amount, is ·355 grm., or 38·55 p. c. silver.

The formula $3\text{CNO}_2\text{ClCy}_2 + 4\text{AgNO}_3$ requires 38·69 p. c. silver, and 9·53 p. c. chlorine.

A compound very similar in appearance is formed with nitrite of silver. It is, however, more stable, sustaining the heat of the water-bath without decomposition.

The original substance, as before mentioned, is very unstable; its watery solution slowly deposits solid products, with evolution of gas-bubbles, and on heating with acids or alkalis, the decomposition is very rapid, and appears to be mainly the same in both cases. When an alkali is used, however, the mixture becomes very dark, and large quantities of the azulmic compounds are formed. The most definite reaction is obtained by heating the

watery solution with a few drops of dilute nitric acid, when it rapidly becomes lighter in colour, and a large quantity of gas is given off with effervescence, the products of the decomposition giving additional evidence of the composition of the substance.

In the remaining solution was found a considerable quantity of oxalic acid, recognized by the usual tests, and by the analyses of a lead and a barium salt.

The gas given off consists principally of carbonic acid and nitrogen, containing also vapour of hydrocyanic acid. After treatment with potash, the remaining nitrogen was found to be slightly inflammable. On passing it over red-hot oxide of copper, water was deposited in the front of the tube, and the gas collected over mercury contained a further quantity of carbonic acid. Another portion passed through an empty tube heated to redness gave a quite appreciable quantity of hydrocyanic acid. From these indications it may be concluded that the inflammability of the gas is owing to the presence of vapour of methylic cyanide.

The following equations represent the two reactions, which appear to take place at the same time :—

In addition to these main products of the action of acids on the substance, I have, by extracting the neutralised solutions with ether, obtained small quantities of at least three solid crystalline bodies containing carbon, hydrogen, chlorine, oxygen, and high per centages of nitrogen; but I can only indicate the existence of these bodies, the separation and purification of which were found to be unusually difficult, both from the nature of the substances, and the very minute quantities formed.

In conclusion, my best thanks are due to Mr. John Williams for the preparation of the greater part of the chloropicrin used in these experiments.