

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.]

THE PREPARATION OF CYANOGEN CHLORIDE.¹

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Berthollet,² in 1787, was the first to prepare cyanogen chloride by the action of chlorine on hydrocyanic acid. Because of his misconception of the nature of chlorine he called the product "oxidized prussic acid," but did not determine its constitution. In 1815 Gay-Lussac³ determined its chemical nature, assigned the formula which is accepted to-day, and named it "chlorocyanic acid." His method was to saturate an aqueous solution of hydrocyanic acid with chlorine and remove the excess chlorine by shaking with mercury. The product was at first obtained from the solution by distillation, but as it was thought this heating decomposed it, in later experiments it was separated by reducing the pressure in the flask until the "chlorocyanic acid" was vaporized. Gay-Lussac found later that he could prepare the substance by the interaction of moist hydrocyanic acid and chlorine and by the action of chlorine on dry mercuric cyanide in the sunlight, but he preferred the first method. He did not purify his product well enough to make an accurate determination of its physical constants. From its behavior he concluded that while at ordinary temperature and pressure it appeared to be a gas, this property might be due to the presence of some other gas such as carbon dioxide. Serullas,⁴ in 1827, found that the presence of moisture greatly facilitated the reaction between the chlorine and mercuric cyanide; enough water was added to the mercuric cyanide to moisten but not dissolve it. Chlorine was passed into the flask containing the cyanide until most of the air was expelled and the flask was then set aside for from 10 to 12 hours, as it was found that under these conditions direct sunlight was detrimental to the reaction. The product contained hydrochloric acid, cyanogen and chlorine. He found the melting point to be -18 to -20° and the boiling point -12° to -15° , but the product was obviously far from pure. He was the first to name it cyanide of chlorine.

Serullas found that while dry cyanogen and chlorine did not react even in the sunlight, the presence of a little moisture resulted in the formation of a yellow liquid. He also found that pure hydrocyanic acid and moist chlorine, when the latter was not in excess, reacted in the sunlight to give ammonium chloride and the yellow liquid. The yellow liquid had a sharp and irritating odor, was insoluble in water, but soluble in alcohol.

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² *Ann. chim. phys.*, [1] 1, 35 (1789).

³ *Ibid.*, [1] 95, 200 (1815).

⁴ *Ibid.*, [2] 35, 291, 337 (1827).

Water slowly decomposed it, giving hydrochloric acid, nitrogen, carbon dioxide and a white crystalline solid which he concluded was a chloride of carbon, since it gave chlorine and carbon on decomposition. From these facts he concluded that the yellow liquid was a mixture of nitrogen chloride and carbon tetrachloride formed by the action of chlorine on cyanogen chloride in the sunlight and attributed the unusual stability of the nitrogen chloride (which did not explode) to the presence of the carbon tetrachloride.

In 1847 Wurtz¹ treated a dilute solution of hydrocyanic acid cooled to 0° with chlorine. After some time a liquid layer formed on the surface of the solution. This layer, after separation and washing with water, boiled at 20° and its vapors burned with a violet flame. He called this liquid "chlorohydrure de cyanogene" and gave it the formula 2CNCl.HCN . When cooled and treated with mercuric oxide to remove the hydrocyanic acid, it decomposed, giving cyanogen chloride, which could be distilled through calcium chloride. When this product contained any excess hydrocyanic acid and chlorine it polymerized to cyanuryl chloride but would not change if entirely pure.

Wurtz determined the boiling point to be 16° and the melting point -7° and considered it a liquid isomer of the gaseous cyanogen chloride. In a later investigation² he found the boiling point to be 15.5° and melting point -5° to -6°. These later observations were confirmed by Salet³ in 1865.

An investigation carried out by Naumann and Vogt⁴ in 1870 showed that the product first formed when chlorine was passed into the solutions of hydrocyanic acid was not a compound of cyanogen chloride and hydrocyanic acid, but simply a mixture of these two substances of no fixed proportions.

In 1850 Wöhler⁵ prepared cyanogen chloride by adding a slight excess of mercuric cyanide to a saturated solution of this salt in water, and passing in chlorine until the solution was saturated and the space above the liquid was filled with the gas. The flask was then closed, placed in a dark room, and shaken frequently until all the cyanide had dissolved or all the chlorine had been used up. Any excess of chlorine was removed by mercury. The cyanogen chloride was then distilled off through calcium chloride and condensed in a U-tube surrounded by a freezing mixture.

In 1854, Cahours and Cloez⁶ described a method which differed from

¹ *Compt. rend.*, 24, 436 (1847); *Ann.*, 64, 307 (1847).

² *Jahresber.*, 1851, 379.

³ *Compt. rend.*, 60, 535 (1865).

⁴ *Ann.*, 155, 170 (1870).

⁵ *Ibid.*, 73, 220 (1850).

⁶ *Compt. rend.*, 38, 354 (1854); *Ann.*, 90, 97 (1854).

the Wöhler method in that a dilute solution of mercuric cyanide was used (100 g. in 4 liters of water) and the chlorine was removed from the product by passing the gas through a tube containing copper turnings.

Langlois,¹ in 1861, used alkaline cyanides in place of mercuric cyanide but found that the action of chlorine evolved so much heat that the temperature rose to 85° or 90°, forming ammoniacal vapors and a black substance. However, by cooling the cyanide solution with ice only a slight brown coloration appeared. The greater part of the cyanogen chloride distilled off at the temperature of melting ice, but some remained behind, forming, according to the author, a compound with the potassium chloride. By heating in a water-bath at 45° to 50° this compound was broken down and the cyanogen chloride was distilled off through a tube containing calcium chloride and copper turnings and condensed in a freezing mixture.

In 1866 Gautier² described a method for preparing each of the supposed 3 forms of cyanogen chloride (gaseous, liquid and solid). He attempted to explain the fact that the gaseous cyanogen chloride of Serullas and the liquid form of Wurtz had the same formula by assuming the former was only the vapor of the latter. It is interesting to note that this crude explanation found its way into one of the text-books on chemistry.³ It was characteristic of all 3 methods that the chlorine was added to the cyanide. In 1895, Hantzsch and Mai⁴ reversed this procedure. To a saturated solution of chlorine in water at 0°, potassium cyanide was added until the chlorine was completely used. The solution was then resaturated with chlorine and the addition of potassium cyanide continued. By always keeping the chlorine in excess the authors claimed to have overcome the tendency of the reaction mixture to turn brown, which always happens when chlorine is passed through a solution of potassium cyanide, with consequent low yield of cyanogen chloride.

The most recent method of preparation was that of A. Held.⁵ The author claimed that the addition of zinc sulfate to a solution of potassium cyanide made the solution more stable under the action of chlorine. Chlorine was passed into a solution of 4 moles of potassium cyanide and $\frac{1}{3}$ mole of crystalline zinc sulfate in 8 liters of water cooled to 0°, until the cyanide was used up and the white zinc cyanide appeared and then just disappeared. The cyanogen chloride was not distilled from the solution, but a 100% yield was calculated from the quantity of sodium which the cyanogen chloride replaced in an organic molecule to which the sodium was united, such as sodium acetoacetic ester.

¹ *Ann. chim. phys.*, [3] 61, 481 (1861); *Jahresber.*, 1861, 345.

² *Bull. soc. chim.*, 5, 403 (1866); *Ann.*, 141, 122 (1867).

³ Roscoe and Schorlemmer, 1, 668 (1878 edition).

⁴ *Ber.*, 28, 2471 (1895).

⁵ *Bull. soc. chim.*, [3] 17, 287 (1897).

Grignard¹ claimed that the method of Held will yield only 25% of the theory and recommended the method of Dreschel,² which is a modification of the Wöhler method. In this method chlorine was passed into a flask $\frac{1}{2}$ to $\frac{2}{3}$ full of water, cooled in ice-water, until a thick mush of chlorine hydrate was formed. The amount of chlorine added was determined by weighing the flask and contents before and after the addition. Twice this weight of mercuric cyanide was added, the flask closed, and shaken in the dark until all the cyanide was dissolved and the solution was colorless. The cyanogen chloride formed was obtained by distillation. Grignard modified the above procedure by adding an amount of sodium chloride equal to the weight of chlorine to prevent the formation of a chlorocyanide. The time of the operation was about 24 hours.

Experimental.

The first method investigated was that of A. Held,³ but the yields, after several trials, were so small that it was not thought desirable to purify the product. The next method tried was that of Langlois.³ The product was purer than that obtained in the method of Held, but the yield was even less, so this method also was abandoned.

As the presence of water seemed to have a marked influence in causing the blackening it was decided to try the action of chlorine on powdered cyanide without the addition of water.

Solid Cyanide with Sand Diluent.—Fifty g. of finely ground potassium cyanide (Baker & Adamson) mixed with an equal bulk of mediumly fine sand, to serve as a heat-distributing medium, were put in a glass tube of 3 cm. diameter. This tube was about 40 cm. long and surrounded by a bath at a temperature of -5° . Chlorine, washed with water, was introduced at the bottom of the tube, and the gas issued at the top through a tube containing copper turnings and calcium chloride and was condensed in a U-tube, cooled to -18° to -19° .

During the run the cyanide in a portion of the tube which was visibly moist turned a dark brown, but that which was seemingly dry did not change color. No product distilled over until the bath surrounding the sand-cyanide mixture had reached a temperature of about $+2^{\circ}$ or $+3^{\circ}$. The final temperature of the bath, 2.5 hours after starting, was $+9^{\circ}$. 28 g. of a yellow colored liquid was obtained, which is equivalent to a yield of 50%. A repetition of this experiment under exactly the same conditions except that the surrounding bath was not allowed to rise above $+3^{\circ}$ gave an 80% yield. Subsequent experiments under apparently the same conditions, gave variable results, in two cases the yields being 88% and 93%, respectively, and in others as low as 10%.

¹ *Ann. chim.*, [9] 4, 40 (1915).

² *J. prakt. Chem.*, [2] 8, 328 (1874).

³ *Loc. cit.*

It seemed probable that variations in moisture and temperature influenced the yield. Experiments were made to determine the effects of a maximum and a minimum amount of water. 50 g. of cyanide triturated with an equal weight of water was treated in a 500 cc. flask with a current of chlorine, the contents of the flask being cooled in a bath at -5° and constantly stirred. The mixture turned dark almost at once upon the entrance of chlorine, which was passed through the mixture for two hours when there appeared to be no more liquid collecting in the receiver. The flask was then heated in a bath at 45° to distil over any cyanogen chloride remaining. There was obtained 11.5 g. corresponding to a yield of 20.7% of a yellow product, somewhat turbid from the presence of cyanuryl chloride formed by polymerization. The behavior of the reaction was quite similar to that of the Langlois method and the yield was unsatisfactory.

In the next experiment the cyanide was carefully dried at 120° , finely powdered and mixed with an equal bulk of sand previously dried. This was treated with chlorine, dried by bubbling through sulfuric acid, for two hours, in the same apparatus and under the same conditions as previously described for the sand-cyanide mixture. No product was obtained which proved that some moisture was essential for the success of the reaction. Any excess of moisture, however, speeded up the reaction to such an extent as to cause local heating with consequent decomposition, formation of azulmic substances, and diminished yield. The best results were obtained with about 2% moisture. In all the experiments with the cyanide-sand mixture examination of the solid residue after the reaction showed that there were numerous scattered areas of decomposition, undoubtedly due to local superheating and excess moisture, the sand particles not being able to distribute this heat rapidly enough. The excess temperature in the zone of reaction drove out the moisture from some areas and deposited it in the cooler portions where it accumulated and led to azulmic formation and lessened yield.

It seemed desirable to find a diluent that would dissipate the excessive heat of the reaction as fast as formed. Carbon tetrachloride proved to be the most effective agent for this purpose.

Solid Cyanide with Carbon Tetrachloride Diluent.—The procedure finally adopted was as follows: 50 g. (1 mole) of Merck's sodium cyanide fused in lumps, purity 98–99%, was finely pulverized and one g. (2%) of water was added and thoroughly mixed with the cyanide. This mixture was put in a 250 cc. filter flask together with 75 cc. of carbon tetrachloride, just enough to prevent the mass becoming pasty, and cooled to -5° by an outside bath of ice and salt at -10° . Chlorine, bubbled through water, was run into the mixture as rapidly as possible with constant shaking of the flask so that the temperature of the reacting mass was held between

the limits of -5° and 0° , for the most part actually at -3° . The time required for the complete absorption of chlorine under these conditions was about 4.5 hours. The reacting materials assumed a flesh color shortly after the entrance of the chlorine. This color did not change until nearly the end of the chlorine absorption, when it became slightly darker, due to small amounts of the material spattering up out of the cooled zone and thereby undergoing decomposition. The reaction flask was connected by a calcium chloride drying tube filled with fused calcium chloride to a U-tube immersed in a freezing mixture. The receiver was connected to a water bubbler through another chloride of calcium drying tube. When the chlorine absorption was complete, indicated by gas passing through the bubbler on the end of the absorption tube, the temperature in the reacting flask was allowed to rise to about $+10^{\circ}$, at which point the cyanogen chloride began to distil. The distillation was continued with gradual rise of temperature and was completed by surrounding the flask with a warm bath. The heating was discontinued when the temperature inside the flask reached 28° . During the distillation a slow current of chlorine was passed through the apparatus. The cyanogen chloride obtained was slightly yellow in color and weighed 60g., corresponding to a yield of 98% based on 49 g. of pure sodium cyanide.

The carbon tetrachloride used as a diluent was distilled off on the steam bath and measured 77 cc. It was colored slightly yellow and was somewhat turbid from the small amount of water that distilled over with it. This amount was practically quantitative for the carbon tetrachloride and water originally added. It had a strong odor of cyanogen chloride and upon standing some time deposited a small amount of cyanuryl chloride. The residue of sodium chloride, left after the removal of the carbon tetrachloride, was an almost white powder and had the appearance of the original powdered cyanide. It weighed 60.5 g., showing that all the sodium cyanide had been transformed into sodium chloride. Its aqueous solution gave a slightly alkaline reaction and only a faint test for cyanide. These results show that the reaction was practically quantitative. An experiment run at a somewhat higher temperature ($+5^{\circ}$) did not give as satisfactory a yield.

One experiment showed that the process can be carried on without any diluent provided the temperature is kept low enough and the chlorine is supplied only as fast as required. The method used was to expose the finely pulverized sodium cyanide containing 2% moisture in a closed chamber surrounded by a refrigerating atmosphere at a temperature of -18° . The chamber was connected with a reservoir of chlorine under pressure. After 16 hours of contact the cyanide had taken on the appearance of brown sugar and the reaction appeared to be complete. The cyanogen chloride formed was distilled off in the usual manner, giving a

yield of 85%. The smaller yield and greater amount of decomposition which was apparent, showed that this method does not permit of such perfect control as when carbon tetrachloride is used as a diluent. The cyanogen chloride may be freed from any dissolved chlorine by solidifying it and sweeping out the chlorine by a slow current of dry air or by letting it stand in a sealed tube over mercury and subsequent distillation. Thus purified, it formed a colorless liquid boiling at 13° at 748 mm. pressure (thermometer bulb immersed in the liquid) and solidifying at -5° to -6° . Regnault¹ gave the boiling point as $+12.66^{\circ}$ and the melting point as -7.4° . Two vapor-density determinations by the Victor Meyer method gave a molecular weight of 63.6 and 63.8, results which were only slightly higher than the theoretical (61.5).

When pure the cyanogen chloride does not polymerize; the impure products, however, show a varying degree of polymerization, depending upon the conditions. This is especially marked in the presence of small amounts of hydrochloric acid, traces of which are apt to be formed by the action of the chlorine on organic impurities accidentally present. Whenever such traces of hydrochloric acid are suspected they should be removed by lime or other alkaline agent, as they very rapidly polymerize the cyanogen chloride to cyanuryl chloride as explained by Chattaway and Wadmore.² In the literature³ the statement is made that great care must be exercised when preparing cyanogen chloride as explosions frequently occur. This idea seems to have originated from a brief note of Weith,⁴ who stated that he had often observed explosions of extreme violence when passing chlorine into solutions of mercuric cyanide, he had never observed them, however, when preparing cyanogen chloride by the action of chlorine on hydrocyanic acid. In this connection attention should again be called to the statement of Serullas already referred to in the introduction, that by the action of moist chlorine on an excess of pure hydrocyanic acid in the sunlight he had obtained ammonium chloride and a yellow liquid, which behaved towards water in such a way as to lead him to conclude the yellow liquid was a mixture of nitrogen chloride and carbon tetrachloride, although the nitrogen chloride seemed to be non-explosive.

Because of these statements, it seemed desirable to investigate the cyanogen chloride prepared from solid sodium cyanide as to the possibility of its containing anything of an explosive nature. Ten cc. of a pure sample was cooled nearly to the freezing point and treated with pure dry chlorine. The colorless cyanogen chloride immediately turned yellow and

¹ *J. hresber.*, 1863, 70 and 74.

² *J. Chem. Soc.*, 81, 194 (1902).

³ Roscoe and Schorlemmer, 1905, Vol. 1, 820.

⁴ *Ber.*, 7, 1745 (1874).

the freezing point was lowered to such an extent that the substance could be cooled to -18° without solidifying. After saturation at -18° the solution was allowed to warm to -10° when boiling began, evidently due to the escape of the excess chlorine. 5 cc. of the material thus saturated with chlorine at -10° was treated with a current of pure anhydrous hydrogen chloride at -5° and allowed to stand in a sealed tube for several days when polymerization to cyanuryl chloride was practically complete except for a few drops of a viscous yellow liquid which resisted further polymerization even upon several week's standing. Considerable pressure was found on opening the tube, owing to the chlorine and hydrogen chloride liberated when the cyanogen chloride solvent was converted to the solid polymer. The few drops of viscous oily liquid were unaffected by a drop of turpentine and there was no evidence of nitrogen chloride or other explosive.

In another experiment, 5 cc. of pure cyanogen chloride saturated at -5° with chlorine was exposed in a sealed tube to direct sunlight for 4 days with apparently no change. The tube, when cooled, and opened showed no pressure. The contents was then saturated with pure dry hydrogen chloride as above. Polymerization appeared to be complete after several days. There was slightly more unpolymerized liquid and it was of a less viscous nature than in the first experiment, but there were no evidences of an explosive compound. The fact that it polymerized almost completely removes the possibility of any secondary effect of sunlight.

In a third experiment 5 cc. of pure cyanogen chloride, without previous addition of chlorine, after saturation at -10° with pure dry hydrogen chloride for $\frac{1}{2}$ hour, was sealed in a tube. Polymerization began almost immediately and was complete in about a day. In this case no oily liquid was noticeable and there was no formation of a yellow color.

The results of this investigation seem to show that the method of preparing cyanogen chloride by the action of chlorine on solid cyanide at low temperature and in the presence of slight amounts of moisture, not over 2%, is superior to other methods in ease of manipulation, quantitative yields and purity of product. It may also be concluded that in the preparation of cyanogen chloride by this method nothing of an explosive nature is formed. The yellow color of the impure product is due probably to a solution of chlorine in the cyanogen chloride, which greatly lowers the freezing point and the oily liquid formed after polymerizing the unpurified product may be a lower polymer like the cyanuryl chloride.

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