NEW REACTION TO PREPARE CYANOGEN

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The reaction between hydrogen cyanide and nitrogen dioxide in presence of aqueous cupric solution was studied in the 0° to 100° C. range using a flow system as well as in a closed vessel, and its product gases were analyzed mainly by gas chromatography. The reaction was a stoichiometric one of high conversion (more than 95%) and high yield (95% or higher) at ordinary temperatures and even at 0° C. It can be used in the industrial production of cyanogen. In this reaction, if economical production is the goal, conditions to avoid the secondary reactions $C_2N_2 + H_2O = HOCN + HCN$, $HOCN + H_2O = CO_2 + NH_3$, $2\ NH_3 + NO + NO_2 = 2\ N_2 + 3\ H_2O$, and $C_2N_2 + 2\ H_2O = (CONH_2)_2$ must be chosen. These secondary reactions occur more easily as the temperature rises, and the pressure, the pH of the solution, and the contact time between cyanogen and water increase.

SINCE 1815, cyanogen has been studied by many researchers (Brotherton and Lynn, 1959). Studies concerning cyanogen became active after World War II, probably because of the rise of commercial production of hydrogen cyanide. Many patents to manufacture cyanogen, using hydrogen cyanide, have been applied for and issued (Lacy *et al.*, 1946; Mojé, 1955; Hutchings, 1957; Fierce and Millikan, 1958; Fierce and Sandner, 1959, 1961a,b, 1962, 1964; Eubanks, 1960; Vancheri and Mackay, 1960; Geerts *et al.*, 1962; Geerts and O'Malley, 1962; Geerts *et al.*, 1964; Zima, 1959, 1960a,b, 1961, 1962; Zima and Gruber, 1966; Isbell, 1967; Huemer, 1955; Kautter and Zima, 1959; Brotherton and Lynn, 1963; Pfeil *et al.*, 1964; Gruber, 1965; Union Carbide Corp., 1960; Rohm and Haas G.m.b.H., 1963).

The author attempted to find an economical method for cyanogen production and discovered the reaction reported here. When hydrogen cyanide is in contact with nitrogen dioxide in the presence of an aqueous cupric salt solution, cyanogen and nitric oxide (NO) are evolved even at room temperature.

When aqueous potassium or sodium cyanide solution is poured onto cupric sulfate powder, cyanogen is evolved (Brauer, 1963; Welcher *et al.*, 1957; Hahn and Leopold, 1935). This reaction can be written as follows:

$$2\ CuSO_4 + 4\ KCN = 2\ Cu(CN)_2 + 2\ K_2SO_4$$

$$2\ Cu(CN)_2 = 2\ CuCN + C_2N_2$$

However, the interaction between cupric ion and hydrogen cyanide is not completely known. When sufficient hydrogen cyanide is mixed with a blue aqueous solution of a cupric salt, a brown precipitate is formed, which eventually dissociates into cuprous cyanide and cyanogen. When cupric nitrate is used and the quantity of hydrogen cyanide is not large, the reaction is as follows: The brown precipitate redissolves on agitation, and the solution becomes green, indicating the formation of cyanocoordinated cupric ions. After it stands for a long time (sometimes overnight) a white precipitate is formed, and the solution returns to the original blue color. The precipitate is in one case cuprous cyanide, but in another case oxamide only. Formation of oxamide means that hydrogen cyanide is oxidized to cyanogen and then hydrolyzed. But in this case, the oxidizing agent is not the cupric ion. If an equivalent of nitrogen dioxide is added successively as an oxidizing agent to the green solution, the reaction takes place immediately at room temperature, and cyanogen and nitric oxide are vigorously evolved from the solution. This reaction proceeds effectively even at 0° C.

The reaction was discovered when the oxidizing agent of cuprous cyanide was being sought. In a test-tube test, cyanogen was detected by gas chromatography, and the presence of nitric oxide was shown when it came in contact with air to form NO_2.

To ascertain that the cupric solution returned to the original state when the reaction was complete, ultraviolet and visible absorption spectra were used. To ascertain if it was the main reaction, the reaction was carried out in a closed vessel under reduced pressure to make a semiquantitative determination, and the author recognized its potential for cyanogen production.

After these preliminary tests, the reaction was studied using a flow system at atmospheric pressure, as well as the closed system in an autoclave. In addition, interaction between hydrogen cyanide and cupric ion was tested. Through these data, some speculation was also made concerning the reaction mechanism.

Experimental

Caution. *Hydrogen cyanide and cyanogen are both very toxic.* Though cyanogen seems to be less toxic than HCN, its odor is much weaker. As cyanogen cannot be easily detected by its odor, extreme care must be exercised with its use. Hydrogen cyanide and cyanogen were handled in a draft in the experiment.

Table I. Reaction in a Closed Vessel under Reduced Pressure[a]

	Reagents			Catalyst					Products, Mm. Hg					
	HCN, mm. Hg	NO_2, mm. Hg	Total, calcd.	$Cu(NO_3)_2 \cdot 3H_2O$, g.	H_2O, g.		Volume of Flask, Ml.	Reaction Temperature	NO	CO_2	C_2N_2	HCN	Water Vapor, Mm. Hg	Total Pressure, Mm. Hg
1	261	130.5	391.5	0.6	2.5	1	700	Room	106	8	105	...	20	239
2	270	135	405	0.12	0.5	2	690	90° C.	111	9	133	...	20	273
3	422	173	595	0.6	2.5	3	675	Room	131	15	185	14	20	365
4	224	188	412	0.6	2.5	4	660	Room	106	6	104	5	20	241
5	346	180	526	0.6	0.5	5	670	Room	144	13	162	1	20	339

[a] *Pressure was measured and calculated at room temperature.*

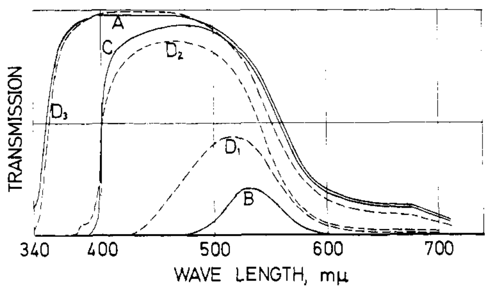

Figure 1. Visible and near ultraviolet absorption spectra

A: 2.4 grams of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 10 grams of water
B: A + 0.28 grams of HCN
C: A + 0.52 grams of NO_2
D: a mixture of B + ½C
  D_1: just after the mixing
  D_2: after 15 minutes
  D_3: after heated to boiling

The heat of formation of cyanogen is extremely high (Pauling *et al.*, 1939), but cyanogen is unexpectedly stable (Welcher *et al.*, 1957), also, against air or oxygen. No explosion or detonation was experienced during the experiment, even when it was mixed with nitrogen dioxide. However, caution must not be neglected when handling it with an oxidizing agent.

Preparation of Hydrogen Cyanide and Nitrogen Dioxide. Hydrogen cyanide was prepared by pouring 50% H_2SO_4 on solid NaCN; the effluent gas was cooled and condensed with ice and water. The collected liquid was dried with phosphorus pentoxide and redistilled to refined hydrogen cyanide. This is the modification of Glemser's method (Brauer, 1963).

Nitrogen dioxide was prepared by dehydrating fuming nitric acid with phosphorus pentoxide, separated from oxygen, and was collected in a trap cooled by dry ice and methanol (Moeller, 1957).

Ultraviolet Absorption Spectra. Near ultraviolet and visible absorption spectra of 1*M* cupric nitrate solution, in which the reaction of hydrogen cyanide and nitrogen dioxide proceeded, were measured by Hitachi EPS-3 spectrometer using a cell of 10-mm. thickness (Figure 1).

Reaction in a Closed Vessel under Reduced Pressure. Using a 500-ml. flask with a stopcock at the top, hydrogen cyanide and nitrogen dioxide were mixed with a cupric nitrate solution. Two small ampoules, containing hydrogen cyanide and nitrogen dioxide, respectively, and cupric nitrate solution of about 0.5 to 5.0 ml. were placed in the flask, which was then cooled to dry-ice temperature and evacuated. At room temperature, the flask was shaken to break the ampoules, and the reaction took place immediately. The pressure inside the flask showed that most of the product gas was out of solution. The procedure was repeated on different concentrations and different molar rations of HCN to NO_2, and in some cases the flask was heated to 90° C. The product gas data at 0° C., measured by gas chromatography, are given in Table I.

Determination of the Products. Gas products were conveniently determined by gas chromatography; oxamide was identified by infrared absorption spectra, and its purity was checked by N-analysis or by volumetric titration

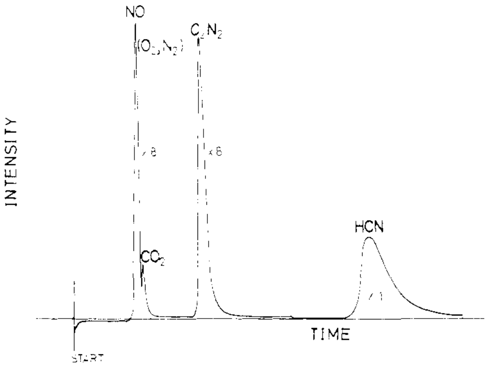

Figure 2. Gas chromatographic chart
Chromosorb P 30/60 + triacetin

of oxalic acid after it was hydrolyzed. Cyanogen and hydrogen cyanide were also determined by titration with silver nitrate using dithizone (Kriedeman, 1964) and nickel glyoximate, respectively, as indicators. The latter is a modified method of Feigl (Feigl and Feigl, 1949; Mojé, 1955).

Gas Chromatographic Determination. A column of 2 or 4 meters in length, packed with 30- to 60-mesh Chromosorb P treated with triacetin (Isbell, 1963), was used to separate the peaks of NO (N_2, O_2), CO_2, C_2N_2, and HCN. Figure 2 is a typical chart written by Hitachi KGL-2B. In this case, when the column length was insufficient or the column became old, CO_2 was difficult to separate fron NO. *Caution must be used for this determination.* To distinguish N_2 from NO, a column packed with molecular sieve 13× (Isbell, 1963) was used (Figure 3).

Determination of Oxamide. A weighed sample of oxamide was hydrolyzed by 0.1*N* caustic soda to oxalic acid, which was titrated by 0.1*N* potassium permanganate solution after it was neutralized with acid.

Titration of Cyanogen and Hydrogen Cyanide. A part of the product gas, whose pressure and volume were measured beforehand, was absorbed into 0.1*N* caustic soda at 0° C. in a closed vessel. CO_3^{-2} was at first precipitated with $Ca(NO_3)_2$ and filtered off. The filtrate was neutralized with HNO_3 and determined volumetrically. One third of it was titrated with $AgNO_3$ using K_2CrO_4 as an indicator. CN^- and OCN^- were measured as the total as silver salts. Another third was titrated with $AgNO_3$ using nickel glyoximate as an indicator (Feigl and Feigl, 1949), and the last third with dithizone as an indicator (Kriedeman, 1964). The end point of each of these two shows the content CN^-.

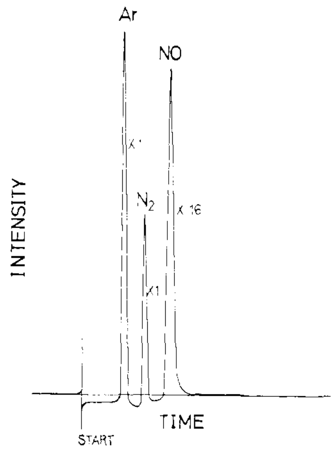

Figure 3. Gas chromatographic chart
Molecular sieve 13×

Qualitative Tests between Hydrogen Cyanide and Cupric Salt Solution. In each of five 100-gram solutions of 1*M* cupric nitrate 5.4, 2.7, 1.35, 0.67, and 0.0 gram of hydrogen cyanide were added, respectively, and left overnight. In the solutions containing 5.4 and 2.7 grams of HCN, cuprous cyanide was formed; in the solution containing 1.35 and 0.67 gram of HCN, no cuprous cyanide was formed. In the case of the solution containing 1.35 grams of HCN, a precipitate of oxamide was formed and increased from 24 to 48 hours after the addition of hydrogen cyanide; in the case of the solution containing 0.67 gram of HCN, oxamide began to precipitate after three days.

Hydrogen cyanide (1.35 grams) was added to each of three 100-gram solutions of 1*M* cupric salt—$CuCl_2$, $CuSO_4$, or $Cu(NO_3)_2$. The next day, a white precipitate of CuCN was formed in chloride, but in sulfate solution, a brown precipitate was observed. In nitrate solution, oxamide precipitated.

Reaction Using the Flow System. An apparatus was used, consisting of a 200-ml. reactor, a 20-ml. reagent (2 HCN + NO_2) holder, and two 500-ml. product holders, each with a sampling outlet. The two gas holders were connected with a three-way stopcock, which led the product gas from the reactor alternately into each one to be measured and analyzed. Cupric nitrate solution (3*M*, 100 grams) was placed in the reactor, which was cooled in a bath of ice and water, and the air over the solution was purged with nitrogen gas. Three separate mixtures in the liquid phase, cooled beforehand to 0° C. and each consisting of 5.4 grams of HCN and 4.6 grams of NO_2, were poured successively into the cupric nitrate solution with stirring. The color of the solution changed green at once, and then from dark green to dark indigo green; this color was kept until the violent reaction was over. No solid precipitate was formed during this time.

The volume of the product gas was measured by the two gas holders switching alternately one after the other. At the same time, a small portion of each 500 ml. was analyzed by gas chromatography, and the remainder was purged for the next 500 ml. Evolution curves are shown in Figure 4. After 4⅓ hours, stirring and cooling were stopped, and the reactor was left overnight, connected through a gas pipe with one of the holders. The broken lines in Figure 4 show the overnight evolution. The color of the solution returned to the original blue color, and a small quantity of oxamide was observed in the solution, which could be neglected in material balance. Total product gas volume was 14,731 ml. (at 0° C., 1 atm.). Summing up each component in each 500 ml., the following results were obtained. Here N_2 is included in NO. NO, 6918 ml.; C_2N_2, 6633 ml.; CO_2, 439 ml.; HCN, 741 ml. (0° C., 1 atm.). Hydrogen cyanide consumed was 94.9%. The yield of cyanogen against it was 97%; the yield of cyanogen against hydrogen cyanide used was 92%; and the yield of by-product carbon dioxide was 3%. As gas chromatographic analysis values were relatively estimated, they would have to be changed if another component was pres-

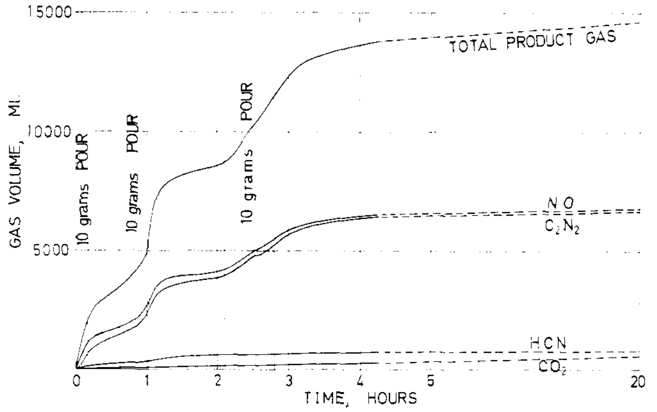

Figure 4. Gas evolution curve

ent, but none was detected other than H_2O, which could be neglected compared with the accuracy of analytical method. Less than 1% of water vapor was there, which was calculated from the vapor pressure of the cupric nitrate aqueous solution at 5° C.

To check the effect of reaction temperature, a similar apparatus was used. A liquid mixture of 5.4 grams of HCN and 4.6 grams of NO_2 was poured at 0° C. into 100 grams of 1 or 2*M* cupric nitrate solution, and after mixing the reagents, the reactor was held at various temperatures. Product gases were measured and analyzed using the method as shown above. When gas evolution almost ceased, analytical values were integrated. Table II shows the results at 0°, 20°, and 60° C. Cyanogen still remained in the solution in these cases, but the concentration of carbon dioxide increased as the reaction temperature rose. In addition, a precipitate of oxamide was observed in the reactor toward the end of reaction at 60° C.

Another apparatus, which can collect the total product gas, was used to analyze it carefully after the experimental operation was over. The apparatus consisted of a 200-ml. reactor, a 40-ml. reagent holder, and a pressure bottle of 25.00-liter volume. The reactor and the pressure bottle were connected with a glass pipe equipped with a gas sampler and a special stopcock, which separated both sides with a pressure difference. Two manometers were attached to the reactor and the pressure bottle, respectively, to show the pressure on each side. At first, the pressure bottle was completely evacuated; 100 grams of 3*M* cupric nitrate solution were placed in the reactor, and the air was replaced by argon gas at atmospheric pressure. The reactor was dipped in a bath and held at about 15° C. during the reaction. A mixture of 16.2 grams of HCN and 13.8 grams of NO_2 was poured dropwise into the reactor, and its pressure was kept at atmospheric pressure; the stopcock was adjusted manually; product gas was collected gradually in the pressure bottle. Sometimes the gas was drawn out through the sampler to check the reaction. When the reaction was almost complete, the reactor was connected to another smaller pressure bottle of 2.67-liter volume through a condenser cooled by chilled water, and left overnight. The gas produced was in a 25.00-liter bottle under 422 mm. of Hg pressure at 22° C. and in the 2.67-liter bottle and the reactor-pipe system (105-ml. overspace volume) under 287 mm. of Hg at 22.3° C. It was analyzed by gas chromatography. In the 25.00-liter bottle there were: NO, $49._4$%; N_2, 0.78%; CO_2, 2.2_7%; C_2N_2, $45._3$%; HCN, 1.8_1%; Ar, 0.79%; and in the 2.67-liter bottle and the reactor-pipe system: NO, $44._2$%; N_2, $13._8$%; CO_2, 7.6%; C_2N_2, $32._7$%; HCN, 0.00%; Ar, 1.5%. Therefore as reaction products, the values of NO, $49._2$%; N_2, 1.7_0%; CO_2, 2.6_5%; C_2N_2, $44._6$%; HCN, 1.6_9% were obtained.

Table II. Effect of Reaction Temperature

Cu^{+2} Concn., Mole/1000 G.	Temp., ° C.	HCN Conversion Ratio, %	C_2N_2 Separated from Liquid, %	CO_2 in Gas, %
1	60	96	72	11
2	20	97	78	4
1	0	98	62	2

Simultaneously, volumetric determination was tried using the titration method. The results were 45.5% (nickel glyoximate) and 45.2_5% (dithizone) compared with 44.6% of gas chromatographic analysis. Using gas chromatographic data, the yield of cyanogen against hydrogen cyanide consumed was 92.2%.

To investigate the pressure effect, the reaction was carried out in an autoclave. Hydrogen cyanide (5.4 grams) and nitrogen dioxide (4.6 grams) were poured onto 200 grams of frozen 1*M* aqueous cupric nitrate solution and kept at 5° C. in an autoclave of 250-ml. volume with stirring. The pressure rose to 9 kg. per sq. cm. in 30 minutes. The product gases were then extracted from the autoclave, while the reaction proceeded, and the cyanogen obtained was 53% against used hydrogen cyanide. The CO_2 content of the product gas was 12%, which was much higher than the reaction at atmospheric pressure; 3.0 grams of crude oxamide were formed which were slightly colored green by cupric salt. Oxamide was identified by infrared absorption spectra.

Hydrogen cyanide (8.1 grams) and nitrogen dioxide (6.9 grams) were mixed with 150 grams of 1*M* cupric nitrate solution in an autoclave as described above. The autoclave was heated to 100° C. The evolution of gas caused the pressure to rise to 69 kg. per sq. cm. Hydrogen cyanide was completely consumed, and a large amount of oxamide and carbon dioxide were produced. There was very little cyanogen in the product gas. The yield was only 1% against used hydrogen cyanide. The same experiment was repeated, and when the pressure rise was stopped at 28 kg. per sq. cm., cyanogen yield was 21%.

Discussion

Through these experiments, especially the flow system, the reaction reported here is recognized to produce cyanogen. Its characteristics are originated from the reaction itself. Copper complex plays an important role. CN^- and N_2O_4 (Addison and Hathaway, 1957) can coordinate on cupric ion, and the reaction probably takes place on the copper ion. N_2O_4 is supposed to dissociate into NO_3^- and NO^+, and these act as oxidizing agents.

Reactions proposed in patents by this time concerning cyanogen production can be classified into five groups: Oxidation of hydrogen cyanide with air or oxygen at high temperature catalyzed by a metal or a metal oxide (Mojé, 1955; Kautter and Zima, 1959; Zima, 1959, 1960a,b, 1961; Gruber, 1965).

Dehydration of hydrogen cyanide at high temperature catalyzed by a metal oxide (Zima, 1960a,b, 1962).

Oxidation of hydrogen cyanide with chlorine, or reaction between hydrogen cyanide and cyanogen chloride (Lacy *et al.*, 1946).

Oxidation of hydrogen cyanide with nitrogen dioxide in gas phase at a temperature between 150° to 650° C. (Union Carbide Corp., 1960; Fierce and Sandner, 1959, 1961a,b, 1962, 1964, Brotherton and Lynn, 1963; Geerts *et al.*, 1964).

Oxidation of hydrogen cyanide with oxygen in the presence of cupric salt solution or cupric oxide suspension (Fierce and Millikan, 1958; Pfeil *et al.*, 1964; Isbell, 1967).

Compared with them, the speciality of this reaction is: a stoichiometric reaction of high conversion and high yield at ordinary temperature—i.e., it is sufficient to react 2 moles of HCN and 1 mole of NO_2 in the presence of Cu^{+2} solution, and at ordinary temperatures, even at 0° C., the reaction takes place smoothly at a conversion rate higher than 95%. It is a homogeneous reaction in solution until the product gases, NO and C_2N_2, bubble out. The unreacted HCN can be discarded, because there is little of it. C_2N_2 may only be separated using some solvent from another main component NO, which is oxidized with oxygen to nitrogen dioxide to be reused. The catalyst in this reaction is the stable cupric ion, whose life is permanent. These are the merits of the reaction for industrial production.

The last reaction group quoted above was represented by Pfeil *et al.* (1964). At first glance, it is very similar to the reaction of this paper but is a different process. In the quoted patent, as the reactivity of oxygen itself is very low, it is necessary to add a large amount of NH_4Cl or pyridine to keep its pH at 2.8 to 3.0 and an accelerator or an oxygen carrier to keep a higher oxygen concentration in the solution. Besides, to carry out the reaction, its temperature must be kept at about 80° C. In the reaction of this paper, no additive is necessary, nor any control of pH during the reaction, because there is no optimum pH value.

Actually, cyanogen dissolves in water, and therefore, when the ratio of 2 HCN + NO_2 to cupric solution is not high, the recovery of cyanogen was low. The first and third flow systems showed that the cyanogen remaining in solution was less than 5%, while in the second flow system it is about 15%. If more 2 HCN + NO_2 is used than in the first and third systems, the ratio of cyanogen remaining in the solution will be much less, and the cyanogen yield is more. The condition of these systems carried out in continuous process will be one of the standard conditions to manufacture cyanogen. In this case, as the molar ratio of HCN to NO_2 is 2 to 1, the quantities of cupric and nitrate ions do not change in the solution, and therefore pH of the solution does not change during the steady pour, except through the effect caused by the increase of water formed by the reaction

$$2\ HCN + NO_2 = C_2N_2 + NO + H_2O$$

and the increment of water is not large. Therefore, 156 grams of 3*M* cupric nitrate solution [56.2 grams of $Cu(NO_3)_2$ in 100 grams of H_2O] can react catalytically with 600 grams of hydrogen cyanide, until it is diluted to 1*M* solution.

However, there are many factors affecting the reaction—namely, temperature, pressure, concentration of cupric ion, concentration of nitrogen dioxide, contact time, and pH of the solution.

The effect of temperature and pressure is discussed in Experimental. The effect of Cu^{+2} or NO_2 concentration will be reported in later papers; these factors are now recognized to affect the reaction velocity. Figure 2 and the results of the third flow system show the increase of carbon dioxide during the last part of the reaction. In this case, the contact time would be the main factor affecting the secondary reaction. The reaction to produce carbon dioxide can be written as:

$$C_2N_2 + H_2O = HCN + HOCN,$$
$$HOCN + H_2O = CO_2 + NH_3$$

In the third flow system, nitrogen is detected in the product gas, and its formation is later than carbon dioxide, as there was more in the 2.67-liter bottle than in the 25.00-liter one. Therefore, the formation of nitrogen is probably given by the formula:

$$2\ NH_3 + NO + NO_2 = 2\ N_2 + 3\ H_2O$$

During the reaction between potassium cyanide and cupric sulfate, which is usually used for the preparation of cyanogen in the laboratory, carbon dioxide is easily formed (Welcher *et al.*, 1957; Woodburn *et al.*, 1949). In this case, the solution is weakly acidic or slightly basic. But in strongly acidic solutions, carbon dioxide is scarcely formed from cyanogen (Travagli, 1936; Fierce *et al.*, 1962; T.V.A. Report, 1962). The same tendency was observed in the experiments reported here. When the cupric nitrate solution was rich in NO_2 and HCN, the formation of carbon dioxide or oxamide was very low, but after the addition of 2 HCN + NO_2 was complete and their concentration decreased, the pH became higher, carbon dioxide was easier to evolve, and oxamide was easier to precipitate.

The qualitative tests suggest that the pH effects the formation of oxamide. When hydrogen cyanide is added to 1*M* cupric nitrate solution (pH = 2.8), its pH becomes lower than 2.0. In the first qualitative test, the nitrate ion acted as an oxidizing agent, which oxidized HCN to C_2N_2, when HCN was 1.35 or 0.67 gram. As the reaction proceeded, the quantity of cyanogen increased in the solution, and the pH gradually became higher to about 2.0. Cyanogen reacts secondarily with water to give oxamide:

$$C_2N_2 + 2\ H_2O = (CONH_2)_2$$

If the quantity of hydrogen cyanide is 2.7 or 5.4 grams, the concentration in solution is higher than in the former case, and under these conditions the oxidizing velocity of nitrate ion would be lower than the velocity to form cupric cyanide. If cupric cyanide is formed, it decomposes to CuCN and C_2N_2, the pH of the solution does not increase but decreases, and the condition becomes difficult for oxamide formation. There is certainly a value of pH above which oxamide precipitates more easily and below which oxamide is difficult to precipitate. In the case of chloride, there is no oxidizing agent; in the case of sulfate, its oxidizing ability is much lower than that of nitrate. Therefore, in both cases, cupric or cuprous cyanide precipitates.

Conclusions

If economical production of cyanogen is the goal, conditions to avoid these secondary reactions must be chosen. Here, only the CO_2 content may be checked in the product gas during the reaction, because the main factor that lowers the yield of cyanogen is the formation of carbon dioxide. Moreover, the ammonia, formed simultaneously with carbon dioxide, can destroy nitrogen oxides to nitrogen and lower the recovery of a useful oxidizing agent.

Patents have been applied for in six countries concerning this reaction; one of these, a British application, was open to public inspection on September 20, 1967, under quoting reference No. 1,084,477.

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