CCVIII.—The Explosion of Acetylene and Nitrogen. Part II.

By WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO.

IN a previous paper (T., 1921, **119**, 1903), a study was made of the fixation of nitrogen which occurs when this gas is exploded with acetylene. During this process, the nitrogen is fixed almost entirely in the form of hydrocyanic acid, the explosion yielding only small amounts of ammonia. The more important reactions in the synthesis of ammonia and hydrocyanic acid were shown to be

and

(1) $H_2 + N_2 + 2C \Longrightarrow 2HCN$ (2) $HCN + H_2 \Longrightarrow NH_3 + C.$

The values of K_1 in the equation $K_1 = [\text{HCN}]^2/[\text{H}_2][\text{N}_2]$ were found to vary from 0.0124 with 4.13 per cent. of nitrogen to 0.0069 with 20.33 per cent. of nitrogen. On the other hand, an empirical relationship, $[\text{HCN}]/[\text{H}_2][\text{N}_2]^{0.37} = K_1^{-1}$, held fairly accurately over the range of concentrations investigated, but no explanation could be given of the physical basis of the equation. Further analysis showed that another equation could be derived from this which was equally applicable. It is possible to replace the concentration of hydrogen by a factor proportional to the area of the carbon surface, for in the experiments previously reported, the atomic concentrations of the carbon and hydrogen in the explosion vessel were identical. Thus $[\text{HCN}]/[\text{C}][\text{N}_2]^{0.37} = K_1^{\text{II}}$. Further experimental work was, however, necessary before a decision could be made as to the relative merits of these two alternatives.

In the study of the reactions occurring in gaseous explosions, the rate of cooling of the gaseous products is a factor of considerable importance and it was desirable to ascertain if K_1^{I} or K_1^{II} held for different rates of cooling of the gaseous products. The evidence already obtained on this point was fairly definite, for in the previous experiments the temperature of explosion and the rate of cooling were progressively altered by the addition of increasing amounts of nitrogen to the explosive mixture, without producing any variations in the value of these constants. Since, however, it was possible that this concordance was accidental, further alterations in the conditions of firing were made by the addition of hydrogen and helium to the mixtures of acetylene and nitrogen. A material increase in the rate of cooling is brought about by the substitution of either of these gases for nitrogen. The thermal conductivities of hydrogen and helium at 0° are 0.0003386 and 0.0003270 respectively, values which are very similar and about six times as large as that of nitrogen (0.000057). Although the effect of these two gases on the rates of cooling will be almost identical, their effect on the temperatures of explosion will be very different. On account of the low specific heat of helium, the temperatures of explosion will be higher in the presence of this gas than when equal amounts of either nitrogen or hydrogen are present.

The substitution of helium for a portion of the nitrogen was found to be without effect on K_1^{I} , although this constant was lowered about 10 per cent. by the addition of 10 per cent. of hydrogen (Table II). If, however, the hydrogen concentration in this equation be replaced by a quantity proportional to the amount of carbon present, as in $K_1^{\Pi} = [\text{HCN}]/[C][N_2]^{0.37}$, where [C] represents the atomic concentration per litre of carbon in the bomb, then it is found that $K_1^{II} = 0.079$ for all of the experiments within experimental error. This agreement suggests that the quantities of hydrocyanic acid produced in these explosions are practically independent of the partial pressures of the hydrogen, being a function only of the carbon surface and the nitrogen concentration. This case is analogous to those observed by Langmuir (Trans. Faraday Soc., 1922, 17, 621) in the reactions between hydrogen and oxygen, and carbon monoxide and oxygen on a platinum surface. It was observed that when either of the two reactants was present in excess the velocity of the reaction was independent of the partial pressure of this reactant and proportional solely to the partial pressure of the other reactant.

The more important reactions, occurring on the carbon surface, may be written

(3)
$$H_2 + 2(\equiv C -) \implies 2(\equiv C - H)$$

(4) $N_2 + 2(-C\equiv) \implies 2(-C\equiv N)$
(5) $HCN + (\equiv C -) \implies (\equiv C - H) + (-C\equiv N)$

The reaction between carbon and hydrogen (3) is more energetic than that between carbon and nitrogen (4). At 800°, the adsorption of hydrogen by carbon is considerable, whereas nitrogen is not appreciably absorbed at this temperature.* At high temperatures (1800-1900°, the temperature of chilling of the hydrocyanic acid reactions), the equilibrium density of hydrogen atoms in the interface will be established with great rapidity, and it seems probable that at high partial pressures the hydrogen atoms will occupy the majority of the free spaces on the carbon surface, and that the density of packing will change only slightly with variations in the partial pressure of the gas. If the formation of hydrocyanic acid occurs between the nitrogen and hydrogen atoms on the surface (5) or on collision between nitrogen molecules and the adsorbed hydrogen atoms, then it would be expected that the rate of formation of hydrocyanic acid would be practically independent of the partial pressure of the hydrogen, a conclusion which is in agreement with the experimental results.

In order to test these ideas still further, the ratio of carbon to hydrogen in the gas mixture was increased by the addition of cyanogen to the acetylene. Owing, however, to the incomplete decomposition of the cyanogen which was present in the cooler regions of the bomb and the production of hydrocyanic acid second. arily by the action of hydrogen on cyanogen, it was impossible to draw any conclusions from these results.

An unexpectedly low result was obtained for the percentage of ammonia produced during the explosion of mixtures containing helium. In the experiments with an excess of hydrogen the average value for $[NH_3]/[H_2][HCN] = K_2$ was 0.51, and the mean for comparable experiments obtained previously (*loc. cit.*) was 0.42. In the helium series, the constant was 0.31, the mean of three experiments (see last column, Table II). It is difficult to ascribe this result to differences between the rates of cooling, or between the temperatures of explosion of the mixtures in the various series. Previous work had shown that the alteration in these conditions brought about by dilution of the acetylene with nitrogen is without appreciable effect on the value of K_2 .

In view of the work of (Sir) J. J. Thomson, it is possible that

* Unpublished experiments by Mr. E. A. Blench,

GARNER AND MATSUNO:

helium acts as a negative catalyst. Positively charged molecules of hydrogen with the noble gases are known to exist under the conditions prevailing in a positive-ray tube. The formation of such a compound between a positively charged hydrogen atom and a helium atom would explain the negative catalysis. If the hydrogen atoms which are active in the production of ammonia are positively charged, then the reduction in concentration of these atoms, occurring on collision with helium atoms, would lower the rate of production of ammonia from hydrocyanic acid or from hydrogen and nitrogen. Experimental work is in progress to test these ideas.

EXPERIMENTAL.

In all, three series of experiments were carried out. Mixtures containing (1) acetylene, nitrogen, and helium, (2) acetylene, nitrogen, and hydrogen, and (3) acetylene and cyanogen were exploded in a spherical vessel at a pressure of approximately three atmospheres. The force of explosion, on account of the dilution with inert gases, was not sufficiently great to cause leaks at the main joint of the bomb, a difficulty which was experienced in some of the earlier experiments. No essential modifications have been made in the apparatus (Fig. 2, *loc. cit.*) or in the experimental procedure, except that it has been found possible to dispense with the bubblers C.

(a) Materials.—The supply of helium was kindly presented by Dr. Travers from a quantity obtained from Prof. Moore, of the Bureau of Mines. This gas was purified by passing over heated copper oxide and through cocoanut charcoal cooled in liquid air. The densities of the gas used in four experiments were 4.008, 3.998, 3.982, and 4.002, respectively. The hydrogen was obtained from zinc and sulphuric acid and was purified over charcoal, surrounded by liquid air. Considerable loss occurred in this process, until the carbon was saturated with hydrogen. Cyanogen, obtained by the action of heat on dry mercuric cyanide (Dixon, T., 1886, **49**, 384), was purified by passing over cotton wool moistened with silver nitrate and dried over phosphoric oxide. The sources of the nitrogen and acetylene have already been given in a previous paper.

(b) Analysis.—When helium was present in the final gaseous mixture, slight alterations were necessary in some of the analytical methods. In the determination of hydrogen by the copper oxide method, owing to the ready diffusion of helium through the quartz tube, it was necessary to replace this material by hard glass. Th analysis of the residue of nitrogen and helium also presented some difficulty. These gases were sparked with excess of oxygen in order to remove the nitrogen, but the results came out too low. On this account it was decided to calculate the percentage of these gases in the final mixture from the initial composition. For this purpose the density of the helium was carefully determined beforehand and accurately known volumes of helium and nitrogen were measured into the bomb.

The cyanogen in the gases was analysed by passing a known volume of the gas through a solution of sodium hydroxide and titrating the solution with silver nitrate by Denigès's method. The analyses by this method were in good agreement with the quantities of cyanogen measured into the bomb. As the gases from the explosion of mixtures of cyanogen and acetylene contained unchanged cyanogen, it was important to devise methods of analysing mixtures containing ammonia, hydrocyanic acid, and cyanogen. The following method of procedure was adopted. The gases were passed through dilute sulphuric acid (N/10) and sodium hydroxide solutions in a series of bubblers, the cyanogen being converted into a mixture of cyanide and cyanate in the alkaline solution. The cyanogen and hydrocyanic acid dissolved in the dilute sulphuric acid were distilled off into a solution of sodium hydroxide and the ammonia in the acid solution was analysed. It has been shown previously that hydrocyanic acid is not appreciably hydrolysed by this treatment. Experiments with cyanogen showed that less than 2 per cent. of this gas was converted into ammonia during the distillation with sulphuric acid. The alkaline solution was titrated for cyanide by Denigès's method. The cyanate in this solution was determined after the removal of the hydrocyanic acid by distillation with excess of dilute sulphuric acid. The residue was treated with more sulphuric acid (Wallis, Annalen, 1906, 345, 357), the cyanate converted into an ammonium salt, and the ammonia analysed by the ordinary methods. 30.61 C.c. of cyanogen gave 28.69 c.c. of ammonia and 28.08 c.c. of hydrocyanic acid. Part of this discrepancy (6 per cent.) was caused by polymerisation of the cyanogen in the presence of mercury in the gas burette. On account of this discrepancy the analysis of the cyanogen in the final gases in Table I cannot be relied on to within 6 per cent. or about 0.02 per cent. of the total volume of gases present. The agreement between the two values for the nitrogen percentage shows that but little error can have occurred in the analysis of the initial gas mixture. As it was decided not to continue these experiments with cyanogen, the cause of the loss of 6 per cent. in the above analysis was not further investigated.

Results.

Table I contains the experimental data, the volume of gases, and the analyses of the initial and final gases. The volume of the gases given in this table is that measured after the explosion, this being the more accurate value, since the gaseous products are more "perfect" than the gases before the explosion. On account of the uncertainty in the values for the compressibility of acetylene, the pressures of the gases measured before the explosion were made use of only as a rough check on the accuracy of mixing of the gases.

Two series of values are given for the percentage of nitrogen; the first is obtained by gas analysis and the second is calculated from the percentage of nitrogen originally present in the bomb; the nitrogen converted into ammonia and hydrocyanic acid is deducted. The former nitrogen percentage is usually somewhat higher (column 16), but the latter (column 17) is the more accurate and is used in the calculations.

The acetylene in the final gases varies between 1 and 4 per cent., and owes its origin very largely to the amount of the explosive mixture which escapes decomposition in the neighbourhood of the walls of the bomb. This conclusion is supported by the results of the explosions of cyanogen and acetylene. In these experiments, 2 to 4 per cent. of the cyanogen and the same percentage of the original acetylene escaped decomposition. The high percentages of the hydrocyanic acid and ammonia in this series are possibly due to direct combination between undecomposed cyanogen and hydrogen.

Comparison of Results.

The effects of the addition of helium and hydrogen to the gaseous mixture of acetylene and nitrogen are summarised in Table II. Here the concentrations of the carbon, hydrogen, and nitrogen are given in gram-mols. per litre. The values from four series are included in this table, (1) the experiments V, VIII, VI, IV, and IX of the preceding paper on the explosion of mixtures of acetylene and nitrogen, (2) the helium series, (3) the hydrogen series, and (4) the cyanogen series.

(a) The Hydrocyanic Acid Equilibrium.—The effect of the replacement of hydrogen by carbon in the relation $[\text{HCN}]/[\text{H}_2][\text{N}_2]^{0.37} = K_1^{\text{II}}$ is shown in columns 5 and 6. The modified expression gives values for K_1^{II} for the first three series which agree within experimental error, the mean values being for (1) 0.0803, (2) 0.0790, and for (3) 0.0775. The addition of 10 per cent. of hydrogen or helium is almost without effect on the latter constant.

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THE EXPLOSION OF ACETYLENE AND NITROGEN.

PART II.

1735

This was not done for the values of K_1^{I} given in the previous paper.

* The concentrations are expressed in gram-mols. per litre.

1736 BROWN: THE ADSORPTION OF URANIUM-X

(b) The Ammonia Equilibrium.—The mean values for $[NH_3]/[H_2][HCN] = K_2$ differ markedly for the different series, being 0.42 for series 1, 0.31 for series 2, and 0.51 for series 3. The addition of helium decreases and the addition of hydrogen increases the value of K_2 . The results of the cyanogen are of doubtful value.

Summary.

Mixtures of acetylene and nitrogen with hydrogen and helium, and of acetylene with cyanogen have been exploded and the products analysed. The yield of hydrocyanic acid is given by the relation $[\text{HCN}] = K_1^{\text{II}}[C][N_2]^{0.37}$. The constant $K_1^{\text{II}} = 0.079$ is found to hold for the experiments previously reported and for the mixtures containing hydrogen and helium. The concentrations of ammonia, produced during the explosion, are given approximately by the equation $[\text{NH}_3] = K_2[\text{HCN}][\text{H}_2]$. K_2 is decreased by the addition of helium and increased by the addition of hydrogen to the gaseous mixture. Helium thus acts as a negative catalyst. The mixtures of cyanogen and acetylene gave larger amounts of ammonia and hydrocyanic acid than those normally obtained; this was accompanied by the presence of unchanged cyanogen in the gases after the explosion.

THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY COLLEGE, LONDON.

[Received, July 10th, 1922.]