THE DECOMPOSITION OF METHANE IN THE NEGATIVE GLOW[1]

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ABSTRACT

The decomposition of methane was studied in the negative glow of a d-c. discharge at pressures of 0.30 and 0.050 mm. The discharge tube was cooled by liquid or solid nitrogen.

The main products were ethane, ethylene, and acetylene in addition to hydrogen and a nonvolatile product which appeared mainly on the cathode as a solid having the formula $(CH)_n$. Smaller amounts of propane, propene, propyne, butane, butene, butadiene, and pentene were also found. Lowering the temperature of the discharge tube from −196° to −210° C greatly increased the amount of ethylene recovered.

The solid product is apparently transported to the cathode in the form of ions and may result from ionic polymerization of the acetylene. Acetylene is the volatile product formed closest to the cathode which suggests that it may also be formed by ionic processes. The formation of the remaining products is consistent with an excitation mechanism in which the C_2 products are formed first and the higher hydrocarbons are formed from them.

INTRODUCTION

The decomposition of methane in the glow discharge has been studied for many years; the early work is summarized in reference 1. More recently, Yeddanapalli (2) studied the decomposition of methane in a d-c. glow discharge using a discharge tube cooled in liquid air. He worked at pressures of a few millimeters and found that the products consisted of ethane, ethylene, and acetylene as well as hydrogen and a nonvolatile product having the formula $(CH_2)_n$. Wiener and Burton (3), using a d-c. glow discharge at atmospheric pressure, showed that under conditions of high conversion and relatively high temperature the only significant products were acetylene, hydrogen, and carbon. McCarthy (4) found that, in addition to acetylene, ethylene and ethane were obtained as products when the gas from a microwave discharge in methane was allowed to impinge directly on a wall cooled by liquid nitrogen.

The low-pressure d-c. glow discharge is suitable for investigations of this type because it permits studying the decomposition in a number of different discharge regions for which the electrical processes are reasonably well understood (5, 6). In addition, the vapor pressures of methane and its decomposition products are such that most of the products can be removed rapidly from the reaction by freezing them out on the discharge tube wall. There is thus the possibility of obtaining direct information about the primary products of the decomposition. This approach was used by Yeddanapalli (2), whose work, however, had two main weaknesses: (*a*) at the temperature of liquid air the vapor pressure of ethylene is sufficiently high that much of it would have remained in the gas phase, and (*b*) his method of analysis was such that the products were determined as acetylene and ethylene with the remainder assumed to be ethane. Any higher hydrocarbons which might have been formed would thus not have been detected.

The negative glow was chosen as a suitable region with which to begin a study of the decomposition of methane in the electric discharge. It was known to be a region of great chemical activity which could be to a considerable degree operated independently of other discharge regions. The experiments reported here were intended primarily to clarify the work of Yeddanapalli and to serve as a basis for a more detailed study of the discharge decomposition. In order to recover the first products more completely, temperatures lower than those in the earlier work have been used. The use of a direct pumping system

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instead of the circulating system previously employed (2) enabled the experiments to be carried out at constant pressure and reduced the residence time in the discharge zone.

EXPERIMENTAL

The experiments were carried out in the apparatus shown diagrammatically in Fig. 1. It consisted of a jacketed discharge tube with a fixed cathode and an anode which could be moved by a rack and gear as shown. The discharge tube diameter of 3.4 cm was chosen as a reasonable compromise between the requirements for efficient trapping of products (small diameter) and ideal glow discharge conditions (large diameter). The electrodes were 3.0 cm in diameter and were made of stainless steel. A mercury diffusion pump with a pumping speed of 10 liters per second and a forepump allowed the system to be evacuated to pressures of less than 10^{-5} mm of mercury. The residence time in the discharge zone with the electrodes placed to include the entire negative glow was 0.05 second for a discharge pressure of 0.3 mm and 0.5 second for a discharge pressure of 0.05 mm. Pressures were measured by a small McLeod gauge.

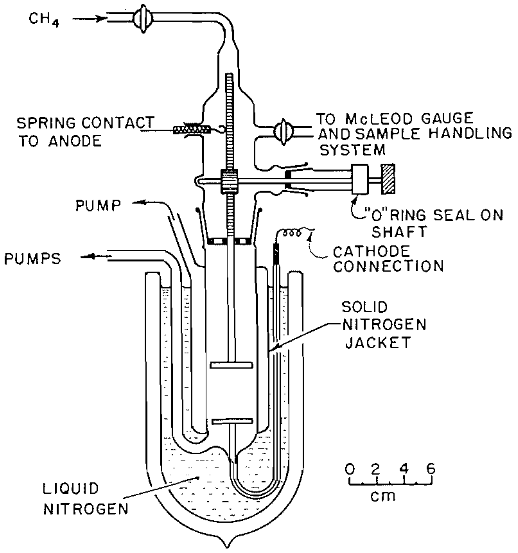


FIG. 1. Discharge tube.

A variable voltage d-c. power supply having a ripple of less than 0.1 volt supplied power to the discharge through a 10,000-ohm series resistor. The discharge current was controlled manually.

The discharge tube was cooled by filling the jacket with liquid nitrogen and pumping on it until the nitrogen solidified. By controlling the pumping speed it was possible to maintain a constant pressure over the nitrogen in the jacket and thus to maintain a constant discharge tube wall temperature for a period of about 15 minutes. Temperatures down to −220° C could be obtained in this way. The temperature of the discharge tube wall was determined by measuring the vapor pressure of methane corresponding to a given jacket pressure and comparing this with the vapor pressure of methane as given by Ziegler (7).

The methane used was Matheson C.P. grade; it was purified by fractional distillation before admitting it to the storage reservoir. Its flow rate was controlled by a needle valve and it was admitted through a trap maintained at either the temperature of liquid nitrogen or the triple point of nitrogen depending upon the methane pressure being used. When necessary a correction was made for the small amount of ethane which was found to be present in blank runs.

The lengths of the negative glow and cathode dark space were determined by measuring the voltage drop across the discharge for various electrode spacings at constant discharge current (5). For the purpose of this work the length of the cathode dark space was taken as equal to the electrode spacing at which the voltage began to rise steeply when the anode was being moved towards the cathode. The anode end of the negative glow was taken as equal to the electrode spacing at which the voltage began to increase when the anode was being moved away from the cathode.

The experiments were performed by cooling the discharge tube to the required temperature, establishing the methane flow, and operating the discharge for a suitable period which in practice varied from 3 to 12 minutes. After the discharge was turned off, the discharge tube was pumped briefly to a low pressure, isolated, and warmed to room temperature. The volatile products were then transferred to a gas burette for measurement and analyzed on a mass spectrometer. The carbon content of the nonvolatile discharge product was determined by oxidizing it *in situ* with an oxygen discharge and measuring the carbon dioxide produced. The method has been described previously (8).

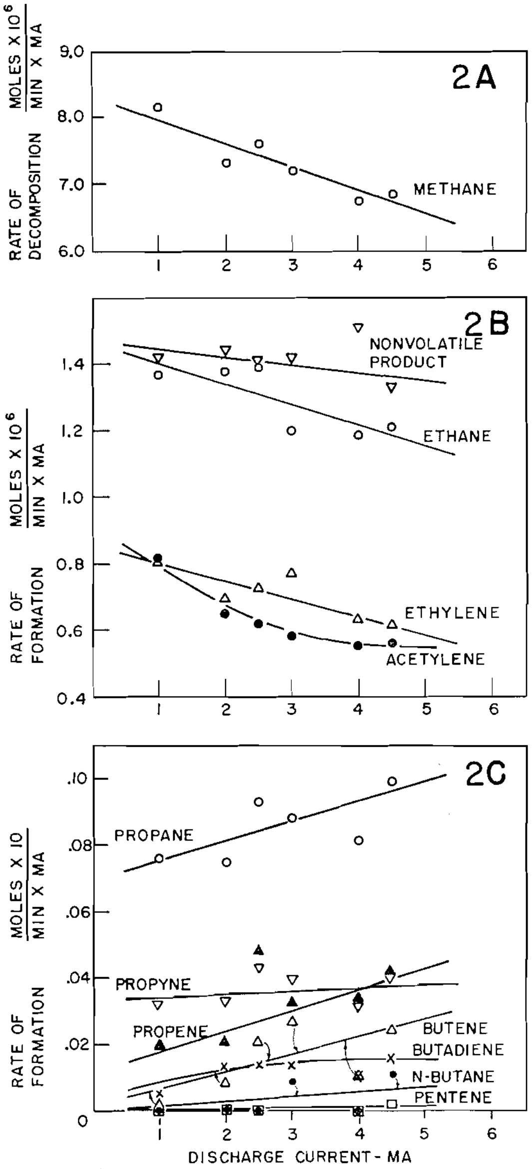
RESULTS

Preliminary experiments demonstrated that the amount of ethylene recovered at about 1% methane decomposition increased nearly 10-fold when the discharge tube temperature was lowered from that of liquid nitrogen ($-196°$ C) to the triple point of nitrogen ($-210°$ C). The amount of ethane recovered also increased by about one-third and some of the higher products, especially propene and butene, decreased in amount. Extrapolation of the existing vapor pressure data for ethylene and ethane (7) indicates that their vapor pressures are less than 10^{-6} mm at $-210°$ C. Thus, the recovery of these products should be practically quantitative at this temperature, assuming equilibrium at the wall.

In several experiments at approximately 2% methane decomposition the gas downstream from the discharge was sampled and analyzed on a mass spectrometer. In each case the amount of hydrogen found agreed, within the accuracy of the analysis, with that calculated on the basis of the products formed.

The variation of the products with discharge current was studied in a series of experiments at a pressure of 0.30 mm, which is the vapor pressure of methane at $-210°$ C. The electrode spacing used was 3.0 cm, equal to the length of the negative glow at this pressure. The results are shown in Fig. 2. The amount of methane decomposed was calculated from the composition of the products; the percentage decomposition was 0.5% for a current of 1 ma. Values shown for the nonvolatile product give its carbon content in gram-atoms. In these experiments the voltage drop across the discharge increased from 330 volts for a current of 1 ma to 390 volts for a current of 4.5 ma.

A pressure of 0.05 mm was chosen as a convenient one for most of the experiments. The choice of a lower pressure made control of the wall temperature less critical and reduced the number of collisions undergone by product molecules in diffusing to the cold wall. In addition, the increased lengths of the cathode dark space and the negative



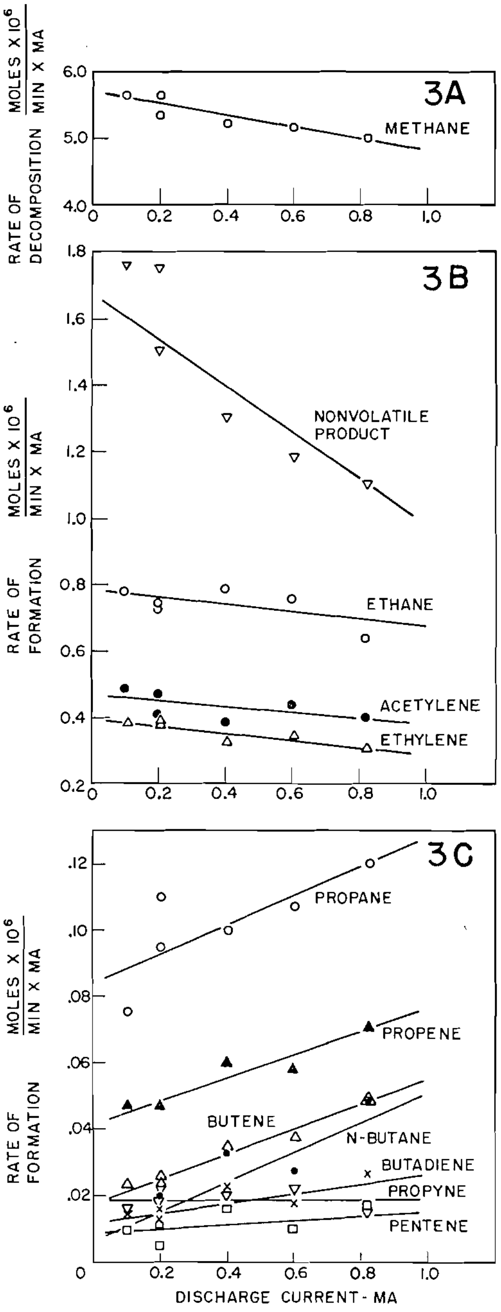


FIG. 2. Effect of discharge current on the decomposition of methane in the negative glow at −210° C. Methane pressure, 0.30 mm. Electrode spacing, 3.0 cm.

FIG. 3. Effect of discharge current on the decomposition of methane in the negative glow at 0.050-mm pressure. Electrode spacing, 10 cm. Temperature, −213° C.

glow made it easier to detect any variation in the products along the discharge. A wall temperature of about −213° C was used in experiments at this pressure.

The effect of discharge current on the rates of formation of the products at a pressure of 0.050 mm is shown in Fig. 3. An electrode spacing of 10 cm was used, corresponding to the length of the negative glow at this pressure. A discharge current of 0.10 ma corresponded to 0.6% decomposition of the methane. The discharge voltage increased from 385 volts for a current of 0.10 ma to 750 volts for a current of 0.82 ma.

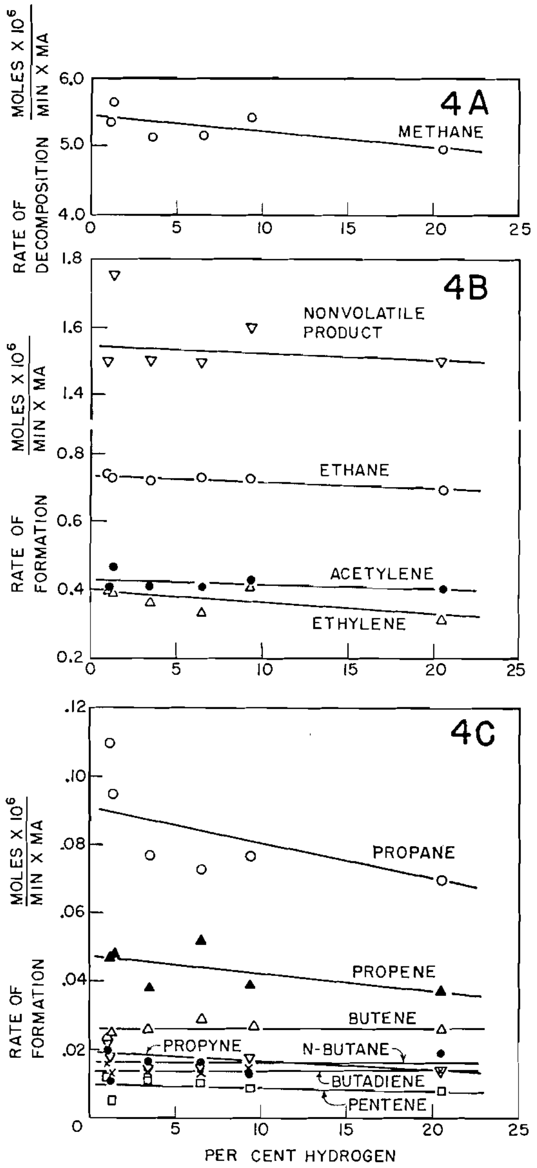
Hydrogen was the only product whose effect on the reaction could be conveniently tested. Figure 4 gives the results of a series of experiments in which hydrogen was added to the methane to give mixtures having total hydrogen contents of up to 20 mole%. The hydrogen formed in the decomposition was taken into account in calculating the compositions of the mixtures.

The distribution of products along the negative glow was studied in another series of experiments in which the electrode spacing was varied. The results are shown in Fig. 5. As the anode was moved towards the cathode the negative glow was eliminated progressively from the anode end. This appeared to have little effect on the operation of the discharge until the edge of the cathode dark space was reached at an electrode spacing of about 1.8 cm. In order to make the experiments comparable over as wide a range as possible a discharge current of 0.50 ma was chosen; lower currents could not be maintained at the smallest electrode spacings used.

The nonvolatile product which formed in the discharge experiments was visible only as a solid deposit on the cathode. This deposit appeared to be a continuous film and interference colors showed it to be of uniform thickness over the area of the electrode covered. In one of the experiments at a pressure of 0.05 mm a flat Pyrex disk having a diameter of 4 mm and a thickness of 0.025 mm was placed on the surface of the cathode. Although a uniform and readily visible deposit was formed on the cathode all around the disk, and extending up to the edge of it, no deposit was visible on the disk itself. It appeared therefore that the deposit was formed only on that part of the cathode which was bombarded by incoming ions.

In order to obtain enough of the cathode deposit for a chemical analysis, several experiments were carried out in which the discharge was operated for periods of about 30 minutes at currents of 7 or 8 ma. The upper electrode was made the cathode in these experiments to facilitate the removal of the deposit. Two samples of about 2 mg each, obtained at the temperature of liquid nitrogen, gave analyses corresponding to $C_{1.00}H_{1.01}$ and $C_{1.00}H_{1.02}$. In another experiment the liquid nitrogen level was maintained about 1 cm below the cathode in order to reduce the possibility that a deposit of frozen product gases was contributing to the formation of the solid. Analysis of this sample gave a composition represented by $C_{1.00}H_{0.75}$. A further sample of the cathode deposit, prepared by operating the discharge at room temperature, was found to have the composition given by $C_{1.00}H_{0.70}$. Although the removal of the solid from the cathode was not quantitative the amount recovered accounted in every case for more than half the nonvolatile product calculated to be formed on the basis of the results in Fig. 2. It seems probable therefore that the cathode deposit accounts for nearly all of the nonvolatile product. The only evidence of any other accumulation of a nonvolatile product was the appearance of interference colors on the anode during these experiments. This may have indicated the formation there of much smaller quantities of another solid product.

It was not possible to determine from the mass spectra whether the product which appeared at $m/e = 42$ was propene or cyclopropane. This product was separated from the others by gas chromatography and shown to be propene.



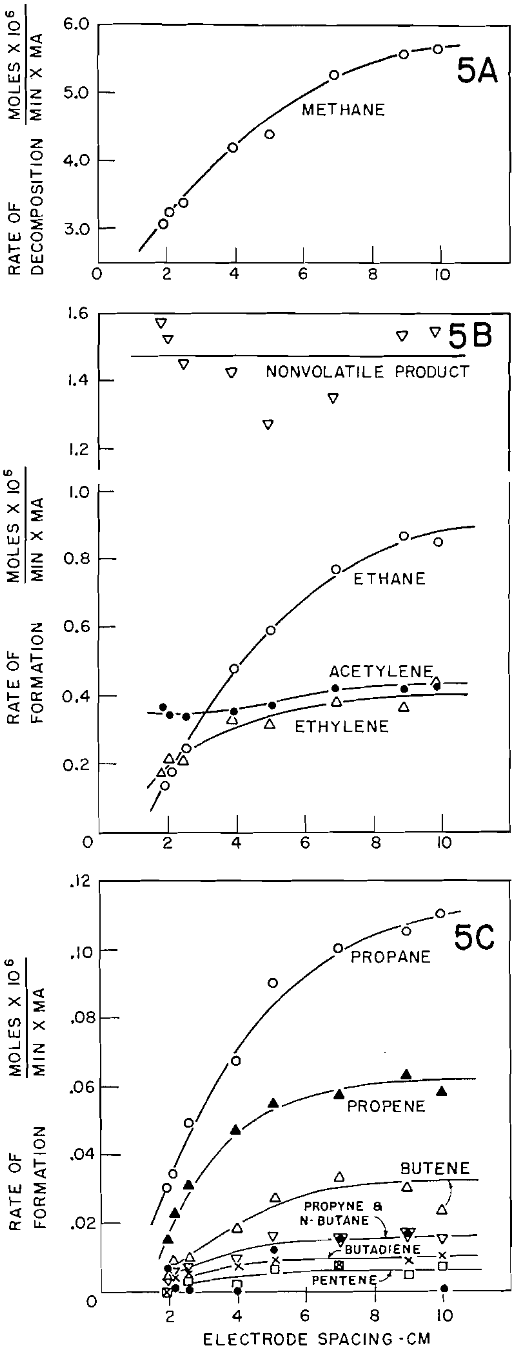


FIG. 4. Effect of hydrogen on the decomposition of methane in the negative glow. Total pressure, 0.050 mm. Current, 0.20 ma. Electrode spacing, 10 cm. Temperature, −213° C.

FIG. 5. Effect of electrode spacing on the decomposition of methane. Pressure, 0.050 mm. Current, 0.50 ma. Temperature, −213° C.

DISCUSSION

The products obtained in this work were considerably more complex than those obtained by Yeddanapalli (2). This was due mainly to the improved analytical technique used. In addition, the increased recovery of ethylene at wall temperatures of −210° C or lower indicates that the yield of ethylene found by Yeddanapalli was too low because much of it would not have been removed from the reaction at the temperature of liquid air. Instead of a polymer having the formula $(CH_2)_n$ as indicated by Yeddanapalli's results, the nonvolatile product was found to consist mostly of a solid of formula $(CH)_n$ which appeared on the cathode.

Yeddanapalli's conclusion that the rate of decomposition in the negative glow is proportional to the current and independent of the pressure holds only approximately for these experiments which extend into the abnormal discharge region. The electron efficiency in this work is defined as the number of methane molecules decomposed per electron charge carried by the current. In the experiments at 0.30-mm pressure (Fig. 2), for which the discharge is nearly normal, the electron efficiency decreases from 12.8 at 1.0 ma to 10.7 at 4.5 ma. At 0.050 mm where the discharge is more abnormal the electron efficiency decreases from 9.0 at 0.10 ma to 8.0 at 0.82 ma. These values are to be compared with the average value of 10 obtained by Yeddanapalli (2) at pressures ranging from 2 to 9 mm and discharge currents between 10 and 30 ma. It is evident that the electron efficiency for the negative glow plus the cathode dark space is approximately 10 over a fairly wide range of discharge conditions.

The products found in these experiments are very similar to those found by Manton and Tickner (9) in their study of the decomposition of methane by a beam of electrons. Since it is known that the electrons in the negative regions of a d-c. glow discharge possess beam properties and have energies similar to those used in the electron beam experiments, this suggests that the products of the negative glow are formed by a mechanism similar to the one which they proposed. The higher electron efficiencies obtained in the glow are accounted for by the many secondary electrons which acquire energy in the electric field, lose it in exciting gas molecules, and subsequently recombine with ions without contributing to the discharge current.

The work of Manton and Tickner indicated that the products were due mainly to excitation rather than to ionization and provided some evidence that the higher products were formed by the reaction of some species, such as excited methylene radicals, with the lower hydrocarbon products. The results obtained here are consistent with this mechanism. In the experiments at both 0.30 mm (Fig. 2) and 0.050 mm (Fig. 3) the yields of the C_2 products fall off with increasing current while the yields of the higher hydrocarbons increase. Also, lowering the discharge tube temperature from −196° C to −210° C while greatly increasing the recovery of ethylene resulted in a decrease in the amounts of propene and butene. Thus, there seems to be definite evidence that the higher hydrocarbons are formed at the expense of the C_2 products.

It has been suggested (10) that the addition of excited methylene to a double bond often results in the formation of an energy-rich cyclic compound which may then rearrange to an olefin. Since no cyclopropane is found among the discharge products there is no evidence of this kind that excited methylene is the active species.

The addition of hydrogen to the methane in concentrations up to 20 mole% appears to have little effect on the products. The small lowering of all yields as the concentration of hydrogen is increased is consistent with the explanation put forward by Yeddanapalli that hydrogen behaves as a diluent, absorbing some of the electrical energy. Since some decomposition of the hydrogen into atoms would be expected, it seems probable that under our conditions of fast trapping the reactions of hydrogen atoms do not play an important part. It is possible, however, that the number of hydrogen atoms generated from the added hydrogen is small compared with the number formed in the methane decomposition and that for this reason the effect of the added hydrogen is not appreciable.

The results obtained by varying the distance between the electrodes (Fig. 5) indicate that the products are not formed uniformly throughout the negative glow. While it is possible that moving the anode into the glow may alter the mechanism it seems to be accepted (5) that the operation of a discharge is disturbed to a relatively small extent until the anode reaches the cathode edge of the glow. Judging by the observed current–voltage relationship this seems to hold true for these experiments. Thus, there appears to be good evidence that most of the acetylene, and possibly part of the ethylene, are formed either at the edge of the negative glow nearest the cathode or, perhaps, in the cathode dark space. The other products appear to be formed in the body of the glow although the results in Fig. 5 may indicate that the distribution is not the same for all of them.

It seems likely that the variation in the relative amounts of the various products along the glow is related to the variation in the electron energy distribution. At the cathode edge of the glow a relatively large number of electrons have sufficient energy to ionize but their number falls off rapidly with increasing distance from the cathode. In the interior of the glow, electrons of much lower energy predominate (5, 6). The fact that most of the acetylene is apparently formed in a region in which there are relatively large numbers of high-energy electrons appears to indicate that it depends on ionization for its formation. This would not be inconsistent with the findings of Manton and Tickner (9) because acetylene constituted a relatively small part of the total product on which their conclusions were based. The remaining products are formed in the interior of the glow where excitation processes are more important. Thus, with the possible exception of acetylene, the mechanism put forward by Manton and Tickner seems to offer a reasonable explanation of the products of the negative glow.

The conclusion that acetylene was the product formed nearest the cathode takes on interesting implications when related to the formation of the solid product. At the low temperatures and low currents used in these experiments a solid product having exactly the formula $(CH)_n$ formed in visible quantities only on the cathode. Since no deposit formed on an insulator covering part of the cathode surface it seems likely that the solid layer was formed by the incoming ions. This conclusion is consistent with the observation that the rate of formation of the nonvolatile product was affected little by changes in wall temperature, pressure, or electrode spacing as shown in Figs. 2 to 5. Experiments in which the cathode was kept above the liquid nitrogen level or in which the discharge was operated at room temperature indicate that the deposit did not originate in a layer of acetylene frozen out on the cathode surface. Instead, these experiments provide some evidence that at higher temperatures the cathode deposit loses hydrogen under ion bombardment. These considerations lead to the conclusion that the solid product on the cathode is an acetylene polymer similar to the cuprene formed in the high-energy irradiation of acetylene (11, 12). There is a considerable amount of evidence that the cuprene formed in these irradiation studies depends on ionization for its formation (12, 13, 14). It seems possible therefore that in the glow discharge acetylene formed near the cathode becomes ionized, either directly or by charge exchange, and then polymerizes in a series of ion–molecule reactions while on its way to the cathode.

The appearance of traces of an involatile product on the anode may indicate that small amounts of a polymer are also formed by another mechanism.

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