THE REACTION OF ATOMIC HYDROGEN WITH CARBON

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ABSTRACT

A thermally produced beam of atomic hydrogen was reacted on a carbon target at temperatures between 30-950°C. The reaction products were isolated on a liquid helium cold finger and subsequently analyzed by gas chromatography. Over the temperature range examined the major reaction products were: $CH_4 \approx 91\%$, $C_2H_6 \approx 8.4\%$, $C_3H_8 \approx 0.6\%$. C_2H_4, C_3H_6 and C_4 hydrocarbons were minor constituents, if formed at all. Hydrocarbon formation increased with temperature, no maximum in the yield occurring at about 770°K as reported in previous studies. The methane yield-temperature dependence showed three distinct phases and activation energies were obtained. At 30° and 950°C, about 1% and 3% respectively, of the available H atoms reacted with carbon to form hydrocarbons.

INTRODUCTION

The discovery that H atoms react with carbon was made by Avramenko (1) in 1946. To date the results of ten other studies have been reported (2)-(11). In all but one investigation, H atoms were produced by electric discharge techniques; the one exception (7) using thermal methods. Chemical analyses of the reaction products were attempted with varying degrees of sophistication in all except one study (5). Agreement between the different investigations as to the hydrocarbons formed in the H atom-carbon reaction is not good, some or all the following have been reported: CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and various butanes and butenes. Several authors believe that methane is the primary reaction product, with higher hydrocarbons resulting from hydrogen abstraction reactions and free radical recombination processes. There is some indication that the formation of acetylene and ethylene may be associated with ionic species formed in the electric discharge used to produce the atomic hydrogen. In some of the experimental studies the products reported as being formed in the H atom-carbon reaction could also have arisen by H atom attack on organic materials, vacuum grease and O-rings, which were part of the system. Most investigations of the H atom-carbon reaction were made at ambient temperatures, but in two cases (8,9) where an extensive temperature range was investigated, a maximum in

the hydrocarbon yield was reported at 770 $\pm$ 50°K. In two kinetic studies (6,9) on the reaction, data were obtained for the rate of carbon removal as a function of temperature and H atom concentration, but no effort was made to correlate these data with the hydrocarbon production.

In this investigation, the H atom-carbon reaction has been re-examined in an effort to determine; 1) the nature of the hydrocarbon products, 2) the yields of hydrocarbon products as a function of temperature and, 3) the efficiency of conversion of atomic hydrogen to hydrocarbons.

EXPERIMENTAL

In designing the experimental arrangement for studying the H atom-carbon reaction, an effort was made to avoid some of the features which may have vitiated the results obtained in previous studies. E.g. Possible pyrolysis of the reaction products, reaction between H atoms and O-rings or vacuum grease, and reaction between hydrogen ions and carbon. To attain these goals, a low pressure atomic hydrogen beam carbon reactor was constructed utilizing a liquid helium cold finger to remove reaction products. This is shown schematically in Figure 1. All materials used in the construction of the reactor were either metal, (copper, brass, Kovar and stainless steel) or glass. Demountable joints were soft soldered using an inorganic flux and all surfaces were acid cleaned prior to assembly. A mechanical vacuum pump

and oil diffusion pump were used to evacuate the system, and pressures in the 10^{-6} mm range were routinely achieved.

Hydrogen atoms were formed by thermal low pressure (10^{-7}-10^{-5}) atm. dissociation of molecular hydrogen in a tungsten effusion tube. The effusion tube, 0.067" O.D. and 0.030" I.D. was heated over 2" of its length to a temperature of 2600 $\pm$ 50°K by electrical induction. The temperature was measured with a Leads Northrop optical pyrometer with emissivity corrections being made. To increase the probability of equilibrium being attained within the tungsten effusion tube for the chemical reaction $H_2 \xrightarrow[\text{Temp.}]{\text{High}} 2H$, three tungsten wires about 1" long and 0.010" diameter were inserted into the bore of the tube to help increase residence times. Matheson Research Grade hydrogen was used in the study and was stored in a glass vacuum line prior to use. The flow rate of hydrogen to the effusion tube was controlled by varying the gas pressure across a fixed leak. Hydrogen flow rates to the effusion tube varied from 0.5 to 9 x 10^{-5} moles hour^{-1}. In most experiments a rate of 2 x 10^{-5} moles hour^{-1} was used. The amounts of gas being fed to the reactor were determined from P.V.T. data using standard vacuum line techniques. These hydrogen flow rates correspond to pressures of the order 5 x 10^{-7} to 2 x 10^{-5} atm at the lowest and highest flow rates, respectively. At the most commonly used hydrogen feed rate (2 x 10^{-5} moles hour^{-1}) the pressure in the effusion tube was approximately 4 x 10^{-6} atm. Using data

given in the JANAF Tables, (12) it may be shown that at this pressure the resulting effusate is essentially pure atomic hydrogen. At the highest experimentally used effusion tube pressure (2×10^{-5} atm.) the effusate was $>$98% atomic hydrogen.

The carbon used in the H atom-carbon reaction was obtained from the Ultra Carbon Corp., Michigan. It had a certified purity of 99.9995% and a density of 1.72 g. $cm.^{-3}$ and was in the form of a solid cylinder, 1" long x 1" diameter. In the reactor, the carbon was mounted in a steel holder on the same axis as the tungsten effusion tube and 2-5/8" from it, presenting the H atoms with a flat target surface of 1" diameter. The carbon target, was heated by four Waltow cartridge heaters of 100 watts each, and the temperature controlled by varying the applied voltage across the heaters. A chromel-alumel thermocouple, inserted into the carbon target with the temperature sensing junction about 1/16" from the reaction face, was used to measure the target temperature. The thermocouple output was measured against that of an ice junction using a Leeds Northrop potentiometer. Target temperatures were constant to $\pm$ 2°C in experiments which usually lasted one hour. A maximum target temperature of about 1000°C was possible and prior to use in the H atom-carbon reaction, the carbon was outgassed at 950°C for three days under vacuum.

The glass liquid helium cold finger used to freeze out reaction products was about 2" diameter and had a capacity of

1 liter. To minimize heat leakage it was surrounded by a liquid nitrogen heat shield. All surfaces in the Dewar system were silvered. After an experiment the cryogenic fluids were removed from the cold finger and the system warmed to room temperature. The reaction products were then removed by a Toepler pump and their total volume measured. During this process the temperature of the carbon target was maintained at 200 $\pm$ 20°C to help minimize adsorption of gas. Provision was made in the collection section of the vacuum line to raise the pressure of the collected sample to slightly above ambient. This was done to help improve the reliability of the gas sampling for chromatographic analysis.

Gas samples from the H atom-carbon reaction were analyzed on a Varian-Aerograph gas chromatograph, Model 1800. A 6 ft. long, 1/4" diameter stainless steel column packed with 216 grams of a 'Poropak' Q stationary phase was used for separating the various hydrocarbons. The column was used isothermally (60°C) for the analysis of CH_4, C_2H_4 and C_2H_6. For higher hydrocarbons the column temperature was programmed at 10°C min^{-1} for six minutes and the column then kept isothermal at 120°C. With this chromatograph, the detection of 10^{-11} moles of a simple hydrocarbon was attainable. Prior to every analysis, the calibration of the chromatograph was checked against injections of known volumes of methane and ethylene. In a typical experiment, 0.15 cc of the collected gas from the atomic hydrogen-carbon reactor was injected

into the chromatograph resulting in hydrocarbon yields of the following magnitude; CH_4 = 4-18 x 10^{-8} moles, C_2H_4 = 1-2 x 10^{-9} moles, C_2H_6 = 3-7 x 10^{-9} moles, C_3H_6 = 0.5 - 2 x 10^{-10} moles, and C_3H_8 = 2-5 x 10^{-10} moles. The over-all accuracy of the measured hydrocarbon yields is believed to be about $\pm$ 7%.

RESULTS AND DISCUSSION

Operating Characteristics of the Reactor, Without the Carbon Target

The reactor, without the carbon target in place, was exposed to H atom attack using a hydrogen flow rate to the reactor of $\approx$2 x 10^{-5} moles $hour^{-1}$. The resulting product gases were analyzed chromatographically. The following species were found; CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and traces of butanes and butenes. These findings were surprising since great efforts were made to remove organic materials from all reactor surfaces prior to assembly. The reactor was disassembled and all surfaces inspected and recleaned. On reassembly and subjection to H atom attack, hydrocarbons were again produced. The effect of exposing the reactor to H atom attack over prolonged periods of time was therefore studied. Samples of the reaction products were analyzed periodically.

Data obtained from these experiments are given in Table I. To permit comparison between different experiments, reaction product yields are all quoted in terms of moles of

hydrocarbon formed per mole of molecular hydrogen fed to the reactor at the stated molecular hydrogen feed rate to the reactor. Quantitative yields for the C_4 hydrocarbons are not given in Table I since their amounts were too small for meaningful analysis. In Figure 2 the methane yield as a function of time is presented from the data given in Table I with a hydrogen feed rate to the reactor of 2×10^{-5} moles $hour^{-1}$. It is at once apparent that the yield of methane decreases quite markedly with the number of hours of H atom attack,(conditioning) and after some 60-80 hours appears to reach a constant minimum. The production of C_2H_4, C_2H_6, C_3H_6 and C_3H_8 all showed the same type of behavior as methane with respect to yields as a function of H atom conditioning time. After some 60-80 hours a stable minimum was attained for all species. The reactor was disassembled, inspected, and surfaces cleaned, and re-assembled. The hydrocarbon yield as a function of H atom conditioning time was re-investigated. The same type of behavior resulted as in the prior experiments, a moderate initial hydrocarbon yield,decreasing with time after some 60-80 hours to the same value as obtained previously. Conditioning was continued for a total of 150 hours without any further change in the hydrocarbon yield occurring. In Table II the stable hydrocarbon yields obtained after prolonged H atom conditioning of the reactor are given.

From these data it is necessary to conclude that despite all efforts to maintain reactor cleanliness, the system was contaminated with carbon or organic material. The initial relatively large production of hydrocarbons obtained directly after assembling the reactor could have resulted from hydrogen atom attack on freshly adsorbed carbon species, CO, CO_2 and possibly some hydrocarbons, on the inside of the reactor after exposure to the laboratory atmosphere. The apparently smaller constant yield of hydrocarbons obtained after prolonged hydrogen atom attack suggests the presence of a fairly large though not particularly accessible supply of organic material. There are two possible sources: 1) carbon in the steel used in fabricating some parts of the reactor, and 2) organic material trapped during the formation of the silver reflective coating on the liquid helium Dewar. (The latter coatings are prepared by the reduction of ammonical silver solutions with sugar). In view of the large silvered surface area of the liquid helium dewar $\approx$5000 cm^2, a small amount of trapped organic material in the silver coating could well be the major source of organic contamination in the reactor.

After establishing that a small constant yield of hydrocarbons could be obtained from the reactor on hydrogen atom attack, a few experiments were tried in which the hydrogen feed rate to the reactor was varied from 0.25-9.75 x 10^{-5} moles $hour^{-1}$ and the reaction products analyzed. These data are recorded in Table I. In Figure 3, the methane yield as a

function of the hydrogen feed rate is presented based on data given in Table I. Similar curves also resulted for the other hydrocarbons and for this reason they are not presented individually. From these data it appears that hydrocarbon yields vary by a factor of about eight with respect to hydrogen feed rate, increasing at the lower feed rates and decreasing at the higher feed rates. As noted in the experimental section, over this range of feed rates the hydrogen species leaving the effusing tube are essentially pure atomic hydrogen, with at most a 1 to 2% variation occurring between the lowest and highest flows. Such small changes in the H atom concentration cannot explain the observed variation in hydrocarbon yield as a function of feed rate. At lower hydrogen feed rates, H atom recombination reactions will occur at a lower rate than at higher hydrogen feed rates. It is possible that the decreased H atom recombination rates at the lower feed rates, and hence longer H atom life time increases the probability for H atom surface reactions producing hydrocarbons. A more detailed study of the effect was not undertaken.

A few experiments were tried to determine if significant cracking of hydrocarbons occurred in the reactor on the hot effusion tube. To this end small quantities of methane were introduced into the reactor and allowed to impinge on the carbon target before being frozen out on the liquid helium cold finger. The products were subsequently analyzed.

Within the sensitivity of the chromatographic detection, no noticable cracking of the methane occurred.

The above experiments served to characterized the operation of the H atom reactor. The apparent inability to remove all traces of organic material from reactor surfaces exposed to H atoms was not expected. It is interesting to note that in all previous experimental studies on the H atom-carbon reaction in which hydrocarbon reaction products were analyzed, no reports were made of tests to determine possible hydrocarbon yields in the absence of the carbon target. Sufficient experimental details were given in some of these studies to indicate that H atom attack on O-rings and vacuum greases in the reactor system probably occurred.

H-Atom-Carbon Reaction

The carbon target was placed in the reactor which was then conditioned to H atom attack for some 100 hours. Experiments were then conducted to determine the hydrocarbon yield from the H atom-carbon reaction as a function of temperature, over the range 30°-950°C. Hydrogen flow rates of 2×10^{-5} moles hour^{-1} were used in all experiments. The following hydrocarbons were detected, CH_4, C_2H_4, C_2H_6, and C_3H_8, with possibly minute traces of some C_4 species. The amounts of the latter were similar to those detected in the background yield without the carbon target present and reliable quantitative measurements were not possible. Qualitatively, C_4 hydrocarbon yields were estimated at $<10^{-3}$

of the methane. For the C_1, C_2 and C_3 hydrocarbons, yields for the hydrogen atom reaction with the carbon target were calculated by subtracting the background yield from the total in the sample. This method of calculating the hydrocarbon yield assumes that the background level of hydrocarbons is not affected by the presence of the competing process at the carbon target. This subject will be discussed later.

The data obtained from 25 experiments are shown in Table III. The hydrocarbon yields are presented in terms of moles of hydrocarbon formed per mole of molecular hydrogen fed into the reactor at the stated temperature. In Figures 4, 5 and 6 the data are shown graphically for methane, ethane and propane. The scatter of the individual points on the methane curve shown in Figure 4 may be considered as acceptable in terms of the expected experimental errors, but the scatter of the points on the ethane and propane curves is considerably larger. The reason for the increased scatter in these data points is not certain. It was observed that yields of ethane and propane obtained in a low temperature experiment performed directly after a high temperature experiment appeared to be significantly higher than the yield obtained when performing two low temperature experiments consecutively. This behavior suggests some type of hysteresis effect is occurring which results in these hydrocarbons being more slowly released during sample collection, than the methane. It is probable that these two hydrocarbons are more strongly adsorbed by

the surfaces in the reactor than the methane, and this might account for the rather poor precision of the data. Unfortunately it was not possible to examine this problem in more detail.

The data presented in Table III for yields of ethylene and propene in the H atom-carbon reaction shows in many cases negative values. This situation arises from the mode of calculations of the yield which was explained earlier. The negative values indicate that smaller quantities of ethylene and propylene are being formed in the presence of the carbon target than in its absence, suggesting that the interaction of the H atoms with the carbon target reduces the background yield of these hydrocarbons. From the data presented in Table III for C_2H_4 and C_3H_6, it appears that their respective yields are not noticably temperature dependent. Assuming this to be true, the average yield of $C_2H_4 = -(0.009 \pm 0.039) \times 10^{-3}$, and of $C_3H_6 = -(0.0014 \pm 0.0035) \times 10^{-3}$ moles per mole of H_2 fed to the reactor over the temperature range investigated. The error limits associated with these values are quite large, consequently it cannot be unequivocally stated that no ethylene or propene is formed during the H atom-carbon reaction. However the data do suggest values close to, if not zero, for yields of these two unsaturated hydrocarbons. To add further credence to this conclusion, at the end of the series of experiments the carbon target was removed from the reactor and the background yield of hydrocarbons again determined.

After some 80 hours of conditioning the yields of hydrocarbons were all found to agree, within the experimental error, with the values obtained previously.

Finally in Figure 7 an Arrhenius plot of the H atom-carbon reaction data is presented, based on the methane yields given in Table III. Three distinct reaction regions are indicated. A least squares fit on the data resulted in activation energies for the production of methane of, 4.5 $\pm$ 1.2 kcal $mole^{-1}$, 0.15 $\pm$ 0.05 kcal $mole^{-1}$ and 0.94 $\pm$ 0.20 kcal $mole^{-1}$ in the high, medium and low temperature regions respectively. The precision limits are the standard deviations calculated from the experimental data. No attempt was made to fit the data obtained from the ethane and propane yields to an Arrhenius type curve due their poor precision.

Hydrocarbon Product Distribution

The present investigation has established that the reaction of hydrogen atoms, at an initial temperature of about 2600°K, with a carbon surface at approximately 30°C produces the following saturated hydrocarbons, $CH_4 \approx 91$ mole % $C_2H_6 \approx 8.6$ mole % and $C_3H_8 \approx 0.4$ mole %. These ratios do not appear to vary significantly over the temperature range studied. There is a possibility that very minor amounts of C_2H_4, C_3H_6 and C_4 species may also be formed. In earlier studies on the atomic hydrogen-carbon reaction, Wood and Wise(9) (1969) reported hydrocarbon yields of $CH_4 \approx 91\%$ with C_2 through $C_8 \approx 9\%$; Harris and Tickner (2) (1947) have reported $CH_4 \approx 91\%$ and

C_2 through $C_5 \approx 9\%$. In both these studies low pressure electric discharges were used to produce hydrogen atoms. In the former study, sufficient experimental details were given to indicate that ionic species from the electric discharge probably did not take part in the reaction. The possibility that some H atom attack on O-rings in the system occurred cannot be ruled out. The reported presence, though presumably small, of hydrocarbons in the C_4 through C_8 range suggests, based on the results obtained in this study, that H atom attack on some material other than the carbon target occurred. Lack of experimental details does not allow an assessment of the validity of the results obtained in the Harris and Tickner study to be made. In the study by Gill, Toomey and Moser (7) (1967) low pressure thermally produced hydrogen atoms reacting with various carbons were reported to produce methane yields from 89.4 to 49.8%, with higher hydrocarbins, C_2-C_4 making up the balance. In this study hydrogen atom attack on organic material within the reaction vessel undoubtedly occurred, and these results must therefore be discounted. It is not possible to compare the values obtained for the relative yields of the individual higher hydrocarbons determined in this study, with those of earlier investigations, since either no specific data were given, or in those cases where they were (9), the experimental procedures were obviously unreliable.

It has been suggested that CH_4 is the primary product in the H atom-carbon reaction and that higher hydrocarbons are the result of secondary processes. The latter could be surface or gas phase interactions between H atoms and CH_4 or between radical species, CH_3, CH_2 or CH. In the present investigation, significant quantities of both C_2H_6 and C_3H_8 were formed in addition to CH_4, and although the experimental conditions probably eliminated secondary gas phase reactions, secondary surface processes could certainly have occurred. The possible primary or secondary nature of C_2H_6 and C_3H_8 in the H atom-carbon reaction cannot be determined from data obtained in this study. Had the precision of the yield data for both C_2H_6 and C_3H_8 been comparable to that for CH_4, and reaction studies made with different H atom flux rates, more definite conclusions with respect to this question might have been obtained. Further clarification of this point could probably also have been derived from electron spin resonance and matrix isolation investigations.

The finding that methane comprises 91% of the total hydrocarbon yield in the H atom-carbon reaction in this study and those of Wise (9) and Harris (2) is interesting in that different reaction conditions were used. In this study the initial hydrogen atom temperature before interacting with the carbon target was 2600°K, whereas in the earlier studies hydrogen atom temperatures in the range 300° - 373°K were used. Despite these differences the relative yield of

of methane with respect to the other hydrocarbons remained unchanged, implying that the factors responsible for the observed product distribution are independent of the H atom temperature. Surface controlled phenomena appear to be dominant. The effective hydrogen atom pressure at the carbon target in this study was at least a factor of 10^3 lower than that used by Wise (9) and Harris (2). If gas phase reactions were important in determining the product distribution a noticeable variation between the different investigations might be expected. That this was not the case again suggests that the carbon surface reactions largely control the product distribution.

H Atom-Carbon Reaction as a Function of Temperature

The investigation of the hydrogen atom-carbon reaction as a function of temperature was followed by measuring hydrocarbon yields over the temperature range 300-1220°K. The best data were obtained for methane and showed that the reaction rate increased continuously with temperature over the entire range. Similar trends were found for ethane and propane. In two earlier studies a maximum in the reaction rate at about 720°K (9) and 820°K (8) was reported. The former study was based on the carbon removal rate after H atom attack, while in the latter, the methane yield was used as the rate indicator. These results are in obvious disagreement with those obtained in this study. The maximum was justified in terms of the thermodynamic instability of

methane at about 850°K (8,9) at which temperature its free energy of formation changes from negative to positive. These arguements must be regarded as specious since the thermodynamic instability predicted for methane at 850°K requires H_2 and CH_4 to be at unit fugacity and for carbon to be in its standard state, with a state of thermodynamic equilibrium existing between the three species. Obviously in the H atom-carbon reaction, these criteria for the application of thermodynamic reasoning do not apply, and in fact, the conditions are deliberately chosen so that the results are kinetically controlled. If thermodynamic reasoning in any form could be applied to the reaction, and have any meaning, the system $4H + C = CH_4$ should have been considered. It is easily determined that for this process the reaction at 850°K has a free energy changes of about -160 kcal. Simply, a maximum in the H atom-carbon reaction rate cannot be justified on a thermodynamic basis. It is probable that in the earlier studies pyrolysis of the hydrocarbon reaction products on the high temperature carbon target was responsible for the observed maximum product yield temperature. In the experimental design used in the present study pyrolysis of this type was kept to a minimum by virtue of the high pumping rate of the liquid helium cold finger.

From the Arrhenius plot of the experimental data for methane shown in Figure 7, three fairly well defined different reaction regimes were found; 300 to 500°K, $E = 0.94 \pm 0.20$

kcal mole^{-1}, 500 to 1,000°K, $E_a = 0.15 \pm 0.05$ kcal mole^{-1} and 1,000 to 1,200°K, $E_a = 4.50 \pm 1.20$ kcal mole^{-1}. It should be noted that the data shown in Figure 7 must be considered as a pseudo-Arrhenius plot since the temperatures of the H atoms and the carbon target were considerably different from each other, whereas the simple reaction rate theory assumes equal temperatures for all reactants. Justification for the occurrence of three different reaction rate regions might be possible if data were available on the adsorption characteristics of H atoms on a carbon surface; unfortunately this is not the case. Data on the adsorption characteristics of molecular hydrogen on carbon (13,14) are known. Below 100°K hydrogen is physically adsorbed; between 100 and 550°K, it is only very weakly adsorbed; between 550 and 950°K, slow changes in the adsorption characteristics occur and above 950°K strong adsorption occurs with the equilibrium being rapidly attained. A heat of adsorption of $\approx$50 kcal mole^{-1} was obtained indicating strong chemisorption in this latter region. It is interesting to note that the three different temperature regions for the adsorption of molecular hydrogen on carbon roughly parallel the three different reaction rate temperature regimes for the atomic hydrogen-carbon reaction. It appears highly probable that above 1,000°K the rapid chemisorption of molecular hydrogen and possibly atomic H could be responsible for the increased reaction rate observed in this region.

Although activation energies for the H atom-carbon reaction have been reported (6,9), the values were based on the rate of carbon removal, not on the yield of methane as in this study. Since ethane and propane are produced in significant quantities in addition to the methane, the two sets of activation energies are not strictly comparable. However, in this study the yield of both ethane and propane followed similar trends with temperature as that of methane, and it is possible that the activation energies based on methane yields and carbon removal rates are not too different. Wise (6) has reported activation energies based on carbon removal rates of 9.2 and 7.1 kcal $mole^{-1}$, in the temperature range 365 to 500°K, and 5.15 kcal $mole^{-1}$ in the 450-715°K region. These values are all considerably larger than those obtained in this study. Hydrogen atom temperatures below 370°K were used in the carbon removal rate method of determining activation energies, (6,9) whilst in this study hydrogen atom temperatures of 2600°K were used. The latter have a thermal energy (translational) $\approx$5 kcal $mole^{-1}$ whereas the former have about 0.7 kcals $mole^{-1}$. If the hydrogen atom translational energy is important energetically in the H atom-carbon reaction, then the activation energies obtained in this study should be increased by about 4 kcal $mole^{-1}$ to be comparable with those of the earlier studies. This improves somewhat the agreement between the two different sets of experimental activation energies.

Hydrogen Atom-Hydrocarbon Conversion Efficiency

The data obtained in the present study allow some limits to be placed on the efficiency with which hydrocarbons are produced in the H atom-carbon reaction. In the following calculations it is assumed that all hydrogen fed to the reactor leaves the effusion tube entirely as atoms. From data in Table III, calculations shows that 1 mole of hydrogen atoms formed in the reactor result in the production of about 1.25×10^{-3} moles of CH_4, 1.2×10^{-4} moles of C_2H_6 and 7.5×10^{-6} moles of C_3H_8 at 30°C. If it is assumed that all hydrogen atoms effusing into the reactor can potentially react with the carbon target to produce hydrocarbons then 0.6%, 0.07% and 0.06% of the atoms are utilized to form respectively CH_4, C_2H_6 and C_3H_8. These figures imply that one out of every 140 hydrogen atoms entering the system is involved in the formation of hydrocarbons.

Of course, not all of the hydrogen atoms formed in the reactor have an opportunity to interact with the carbon target. Using molecular beam properties and the geometry of the reactor system, (15,16,17 & 18) it may be shown that between 60-70% of all atoms leaving the effusion tube will interact directly with the carbon target. It is possible that some H atoms interact with the carbon target after undergoing reactor wall collisions. The number of such secondary target collisions is likely to be small since the

target surface area $\ll$ than the total internal surface area of the reactor. Assuming that only those H atoms interacting with the target directly after leaving the effusion tube are likely to produce hydrocarbons, the fraction of atomic hydrogen collision leading to CH_4, C_2H_6, and C_3H_8 is calculated at approximately 1.0%, 0.1% and 0.1% respectively. These numbers imply that about one out of eighty three H atoms colliding with the target produces hydrocarbons. At about 950°C, the hydrocarbon yield values are increased by about a factor of three and hence the collision efficiency of H atoms to produce hydrocarbons becomes about one out of twenty eight H atoms.

It is not possible to compare directly the H atom-hydrocarbon conversion efficiencies obtained in this study with those of other workers, since the data are either not reported, or the experimental conditions are not analogous to those used in the present study. In two studies (9,11),where the latter condition holds, H atom conversion efficiencies were reported of between one and two orders of magnitude lower than obtained in this investigation. It appears probable that the higher hydrogen pressures used in the earlier studies, resulted in experimental conditions in which H atom recombination rates were substantially greater than in the present study with the corresponding dimunition in hydrocarbon forming processes.

CONCLUSIONS

1. The reaction of atomic hydrogen with carbon at 30°C results in the production of $CH_4 \approx 91\%$, $C_2H_6 \approx 8.4\%$, and $C_3H_8 \approx 0.6\%$. The formation of C_2H_4, C_3H_6 and C_4 species in the reaction is zero or close to zero.

2. About 1.2% of the atomic hydrogen interacting with the carbon target is converted to hydrocarbons at 30°C. At 950°C this fraction increases to about 3.6%.

3. Over the temperature range 30-950°C the hydrocarbon product distribution remains essentially unchanged

4. Previous reports of a maximum in the hydrocarbon yield at 720-820°K were not substantiated. The previously reported maximum is believed to be a function of the experimental arrangements.

5. The H atom-carbon reaction rate to produce methane has three distinct phases. Activation energies were determined· 300 to 500°K, $E_a = 0.94 \pm 0.20$ kcal mole^{-1}; 500 to 1000°K, $E_a = 0.15 \pm 0.05$ kcal mole^{-1}; and 1000 to 1200°K, $E_a = 4.5 \pm 1.2$ kcal mole^{-1}.

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TABLE I

EXPERIMENTS TO DETERMINE BACKGROUND HYDROCARBON YIELD DUE TO HYDROGEN ATOM REACTION WITH RESIDUAL CARBON OR CARBON SPECIES IN REACTOR

Expt. No.	H_2 Feed Rate (Moles x 10^{-5}/hour)	Moles x 10^{-3} of Hydrocarbon Formed Per Hour Per Mole H_2 Reacted				
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
52	1.9430	9.4765	1.2666	0.7516	0.0983	0.1629
53	1.9350	3.0493	0.3192	0.1939	0.0147	0.0276
54	1.8917	1.6025	0.0890	0.1266	0.0057	0.0240
55	2.1736	2.2031	0.1710	0.1711	0.0114	0.0303
56	1.9635	1.7013	0.1188	0.1406	0.0076	0.0267
57	1.9293	1.8502	0.1024	0.1196	0.0091	0.0233
58	2.0461	1.2485	0.1344	0.1217	0.0055	0.0192
59	2.0885	1.2118	0.1719	0.1142	0.0056	0.0206
60	1.9907	1.6453	0.0809	0.1457	0.0092	0.0258
61*	0.5061	4.0439	0.6047	0.4110	0.0170	0.0810
62	2.1318	2.0290	0.0813	0.1960	0.0057	0.0337
63*	0.7561	2.5788	0.2263	0.3853	0.0090	0.0677
64*	9.7126	0.3339	0.0127	0.0315	0.0005	0.0052
65*	4.0310	0.5501	0.0401	0.0310	0.0045	0.0052
66*	6.5012	0.7081	0.0220	0.0750	0.0005	0.0049

* These data points were used in establishing the curve shown in Figure 3.

TABLE II

HYDROCARBON YIELD AFTER CONDITIONING THE REACTOR FOR A PROLONGED PERIOD OF TIME (>80 HOURS) AT A HYDROGEN FEED RATE OF 2×10^{-5} MOLES/HR^{-1}

Hydrocarbon	Moles of Hydrocarbon per Mole of H_2 Fed to the Reactor
CH_4	$(1.69 \pm 0.21) \times 10^{-3}$ [a]
C_2H_4	$(1.18 \pm 0.27) \times 10^{-4}$
C_2H_6	$(1.42 \pm 0.20) \times 10^{-4}$
C_3H_6	$(7.5 \pm 1.6) \times 10^{-6}$
C_3H_8	$(2.55 \pm 0.34) \times 10^{-5}$

(a) Reported error limits are the standard deviations of the observed experimental values.

TABLE III

DATA FOR HYDROCARBON YIELDS IN THE TEMPERATURE RANGE 301 TO 1222°K WITH A HYDROGEN FEED RATE OF 2×10^{-5} MOLES $HOUR^{-1}$

Expt. No.	Target Temp. T°K	$I/T°K \times 10^{-3}$	CH_4 Yield* $\times 10^{-3}$	C_2H_4 Yield $\times 10^{-3}$	C_2H_6 Yield $\times 10^{-3}$	C_3H_6 Yield	C_3H_8 Yield	Log_{10} CH_4 Yield
1	1137	0.880	5.950	0.0053	0.595	0.0036	0.0482	0.775
2	983	1.017	4.706	0.0081	0.331	0.0108	0.0252	0.673
3	804	1.244	4.354	0.0046	0.294	-0.0025	0.0275	0.639
4	626	1.597	4.265	0.0483	0.298	-0.0030	0.0276	0.630
5	428	2.336	3.876	-0.0021	0.221	-0.0036	0.0206	0.588
6	1108	0.903	6.460	0.0374	0.648	-0.0003	0.0400	0.810
7	508	1.969	4.000	-0.0068	0.275	-0.0029	0.0225	0.602
8	1206	0.829	7.109	0.0501	0.725	0.0012	0.0548	0.852
9	1075	0.930	5.265	-0.0086	0.400	-0.0029	0.0246	0.721
10	333	3.003	2.838	-0.0540	0.264	0.0037	0.0148	0.453
11	1101	0.908	5.519	0.0262	0.580	-0.0037	0.0311	0.742
12	898	1.114	4.217	-0.0375	0.259	-0.0031	0.0173	0.625
13	301	3.322	2.723	0.0183	-	-	-	0.435
14	1144	0.874	6.188	0.0319	0.664	-	0.0296	0.792
15	370	2.703	3.293	-0.0604	0.215	0	0.0072	0.518
16	352	2.841	3.350	-0.0718	0.199	0	0.0071	0.525
17	305	3.279	2.580	-0.0040	0.201	-0.0019	0.0255	0.412
18	945	1.058	4.470	-0.0565	0.218	-0.0032	0.0093	0.650
19	482	2.075	4.171	-0.0129	0.216	-0.0045	0.0170	0.620
20	770	1.299	4.163	-0.0364	0.208	-0.0016	0.0093	0.619
21	675	1.482	4.130	0.0404	0.241	-0.0022	0.0158	0.616
22	306	3.268	2.399	-0.0318	0.240	-0.0042	0.0239	0.380
23	386	2.590	3.758	-0.0743	0.264	-0.0039	0.0122	0.575
24	1222	0.818	6.814	0.0207	0.536	-0.0023	0.0466	0.833
25	616	1.623	3.932	-0.0648	0.274	-0.0051	0.0100	0.595

* Yields are presented in terms of moles of hydrocarbon formed, per mole of H_2 fed to the reactor.

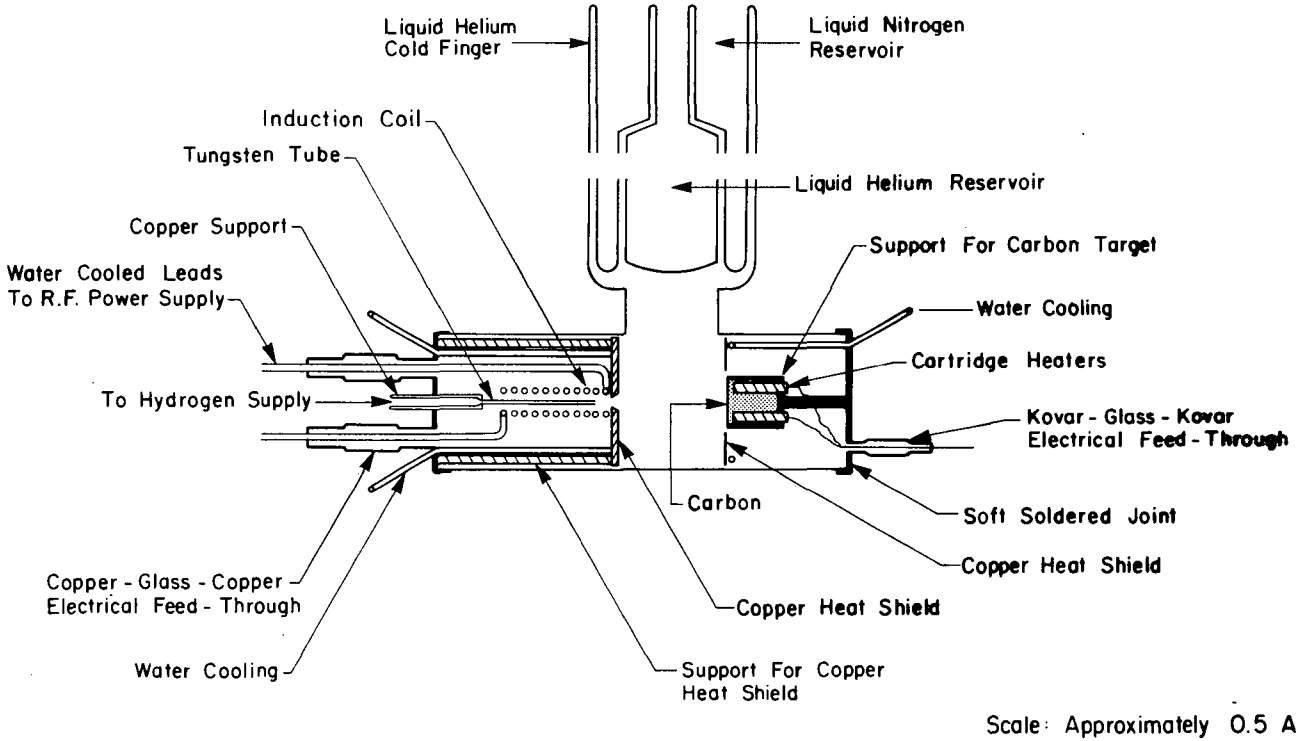

Fig. 1 SCHEMATIC ARRANGEMENT OF ATOMIC HYDROGEN/CARBON REACTION CELL

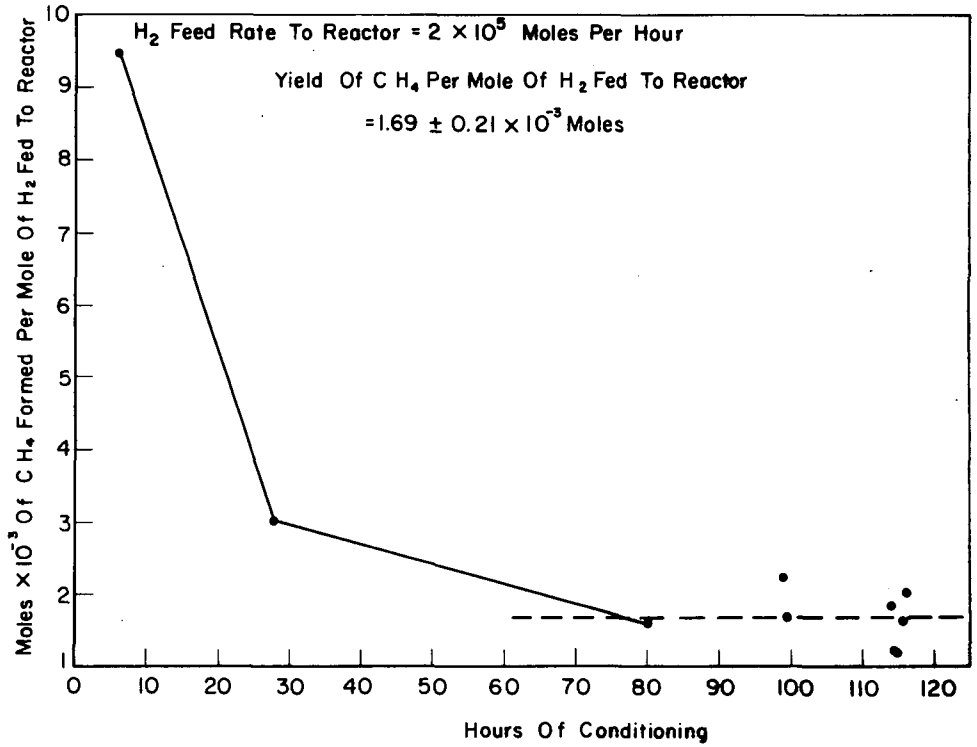

Fig. 2 YIELD OF CH_4 IN REACTOR WITHOUT CARBON TARGET AS A FUNCTION OF H ATOM CONDITIONING TIME

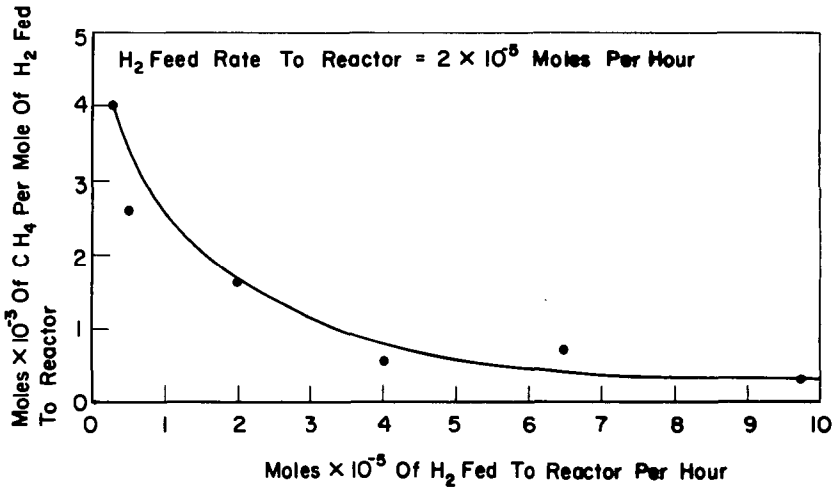

Fig. 3 CH_4 YIELD AS A FUNCTION OF H_2 FEED RATE

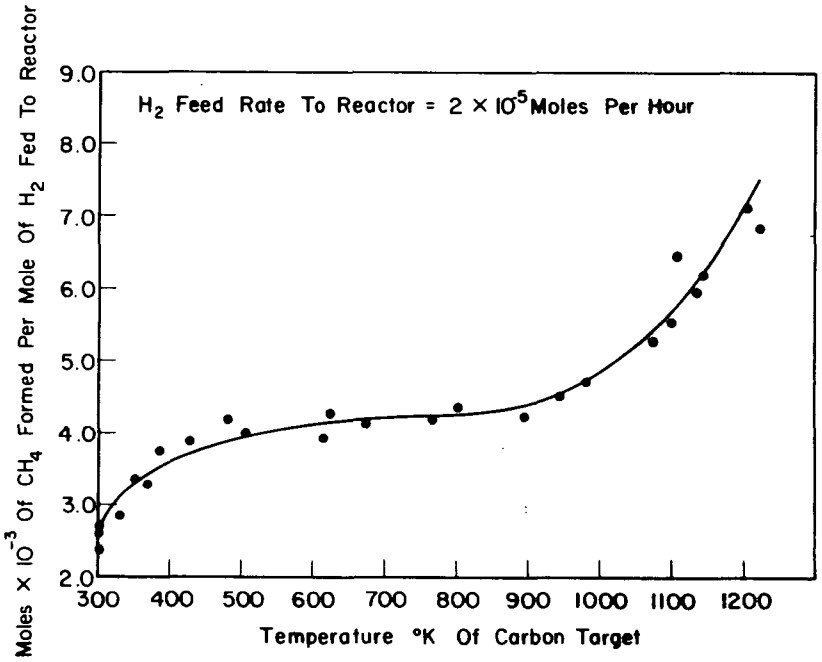

Fig. 4 METHANE PRODUCTION AS A FUNCTION OF TEMPERATURE

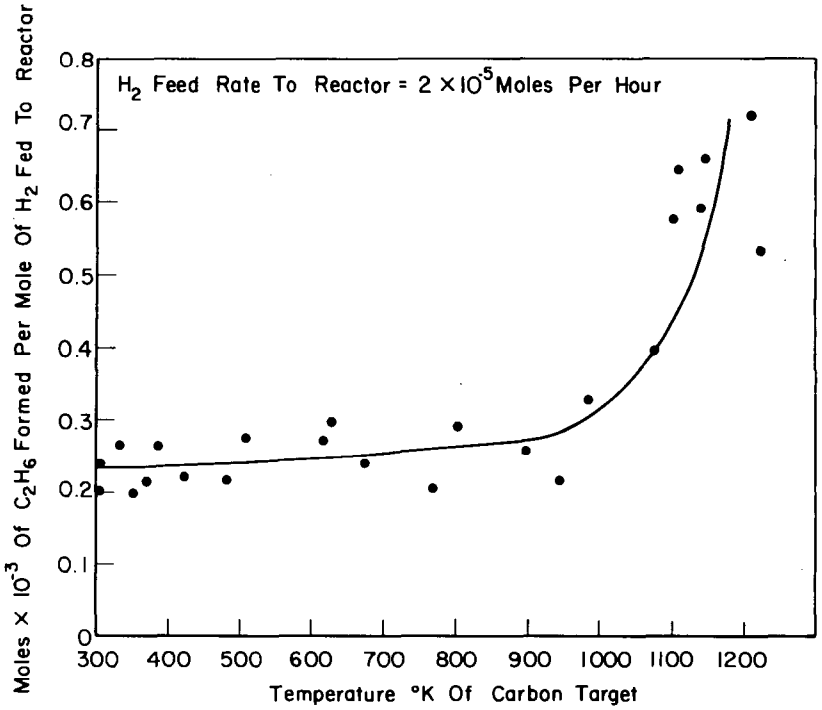

Fig. 5 ETHANE PRODUCTION AS A FUNCTION OF TEMPERATURE

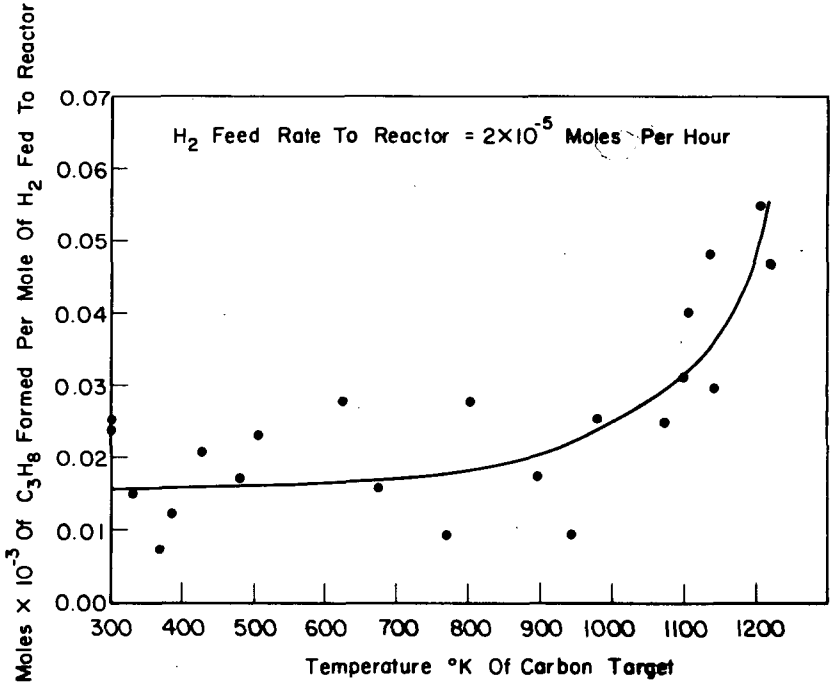

Fig. 6 PROPANE PRODUCTION AS A FUNCTION OF TEMPERATURE

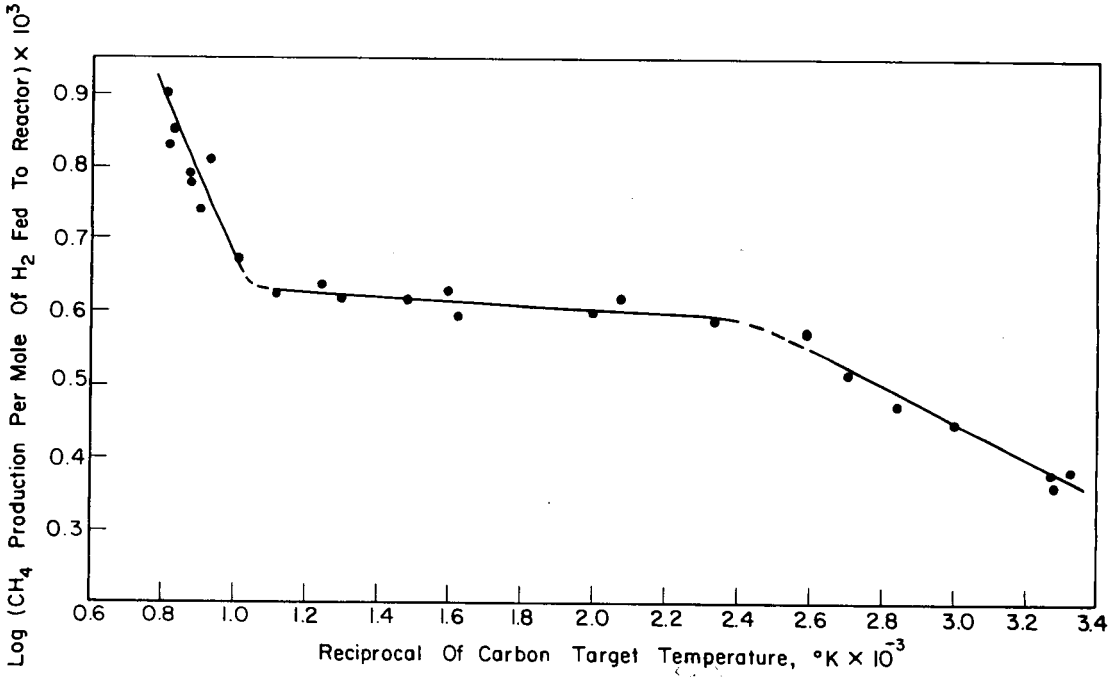

Fig. 7 ARRHENIUS PLOT FOR METHANE PRODUCTION