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# THE REACTION BETWEEN CARBON AND THE PRODUCTS OF HYDROGEN, OXYGEN AND WATER MICROWAVE DISCHARGES

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**Abstract**—The reactions of carbon with the products of hydrogen, oxygen and water microwave discharges have been studied at room temperature and low pressures. The reaction between atomic hydrogen and carbon occurred at an insignificant rate if the carbon was located outside the discharge. Small amounts of hydrocarbons, both gaseous and solid, were observed if carbon was placed directly in the hydrogen discharge. An extensive reaction occurred between atomic oxygen and carbon, when the carbon was either in or outside of the discharge. Carbon monoxide was the major reaction product. The products of a water discharge reacted with carbon giving principally a hydrogen–carbon monoxide mixture.

## 1. INTRODUCTION

THE homogeneous or heterogeneous recombination of many atomic species are well characterized in the literature. The reactions of atomic species with solids to produce a gaseous product are less well characterized, particularly for the case of carbon. Generally, reactions involving atomic species show a negligible temperature dependency over a wide temperature range; hence, the reactions of atomic species with solids should proceed at a rapid rate at low temperatures. SIEGEL[1] has reviewed the results for the case of the reactions of solids with atomic hydrogen. STREZNEWSKI and TURKEVICH[2] have studied the reactions of atomic oxygen with carbon films. BLACKWOOD and MCTAGGART[3, 4] have studied the reactions of carbon with the atomic species produced by passing carbon dioxide, hydrogen, oxygen, and water vapor through an $R_f$ discharge.

The nature of the discharge products varies with the type of discharge used. Although there are many methods used to produce atomic species[5], the microwave discharge seems especially suitable since (a) no electrodes come in contact with the discharge, (b) a very intense localized discharge is produced with little tendency to spread, and (c) stray electrical fields are eliminated by use of a wave guide.

A brief announcement reporting the authors' findings on the reaction of carbon with products of hydrogen, oxygen and water microwave discharges appeared recently.[6] This paper presents a detailed account of these findings.

## 2. EXPERIMENTAL

A controlled gas flow apparatus was used. The mass flow rate was measured from the pressure drop across an orifice as the gas flowed from a 5 l. expansion reservoir to the discharge zone. Pressures were measured on a McLeod gauge (tilting type). A thermocouple gauge and flow meter served merely as qualitative indicators of the constancy of flow rate. Spectroscopically pure graphite rods were suspended vertically in Pyrex tubing (i.d. = 11.5 mm) by lengths of fine Ta wire at varying distances from the discharge.

A General Electric Analytical Mass Spectrometer was used to identify and determine the concentration of the major gaseous products. The mass spectrometer was connected directly to the

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flow system through a Knudsen leak at a distance of ca. 300 cm from the discharge zone.

The power source for the discharge was a Raytheon Diatherm unit (Model CMD 10) with an output of 85 W at 2450 Mc/s. The cavity (air cooled) was also obtained from the Raytheon Co. The power level was maintained at maximum output unless otherwise specified. The discharge was initiated by a Tesla coil. Each gas gave a characteristic luminous emission in the cavity due to finite concentrations of excited species. A typical luminous discharge zone would have the following dimensions: length = 7 cm, diameter = 11.5 mm (i.d. of the Pyrex discharge tube).

Hydrogen was obtained from the Matheson Co. and passed through a De-oxo unit and a liquid nitrogen trap prior to storage. The following impurities were determined by mass spectrometric analysis: trace-$H_2O$; 0.2%-$N_2$. Oxygen was obtained from the Matheson Co. and passed through a liquid nitrogen trap prior to storage. The following impurities were determined: trace-$H_2O$; 0.5%-$N_2$. The vapor of distilled water was used. No impurities were detected. The hydrogen-carbon monoxide mixture used (40–60 mole per cent) was obtained from the Matheson Co. The following impurities were determined: trace-$H_2O$; trace-$Fe(CO)_5$. The iron carbonyl was removed by use of an acetone slurry trap.

## 3. RESULTS

### 3.1 *Hydrogen discharge*

The emission spectrum of the hydrogen discharge showed the Balmer series of atomic hydrogen. A Pt wire glowed red at greater distances from the discharge than where the carbon rod was positioned, indicating significant concentrations of hydrogen atoms recombining on the Pt surface.

Carbon reacted at a negligible rate when located downstream from a hydrogen discharge (hydrogen pressure 0.06 torr, linear flow rate ca. 340 cm $sec^{-1}$), even if the carbon was positioned just outside the luminous discharge zone. On the other hand, when the carbon was directly exposed to the discharge, the reaction proceeded at a significant

TABLE 1. CHARACTERIZATION OF REACTION OF CARBON WITH AN OXYGEN DISCHARGE

| Pressure (torr X$10^2$) | Rod diameter (mm) | Rod length (cm) | Distance, rod from discharge (cm) | Microwave power (W) | Oxygen reacted (%) | Mole per cent in product | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $O_2$ | CO | $CO_2$ | $CO/CO_2$ |
| 6.1 | no rod | — | — | 85 | 9.0 | 92.0 | 4.0 | 4.0 | 1.0 |
| 5.6 | 6 | 13 | 5 cm into discharge | 85 | 96.0 | 1.0 | 91.0 | 8.0 | 11.0 |
| 4.7 | 6 | 13 | 1.3 | 85 | 75.0 | 29.0 | 54.0 | 17.0 | 3.2 |
| 3.3 | 6 | 13 | 6.3 | 85 | 63.0 | 47.0 | 39.0 | 14.0 | 2.8 |
| 4.8 | 6 | 13 | 24.0 | 85 | 32.0 | 69.0 | 19.0 | 12.0 | 1.6 |
| 3.3 | 6 | 11 | 1.3 | 17 | 78.0 | 19.0 | 62.0 | 19.0 | 3.3 |
| 3.3 | 6 | 11 | 1.3 | 85 | 86.0 | 12.0 | 72.0 | 16.0 | 4.5 |
| 3.5 | 6 | 11 | 15.0 | 17 | 49.0 | 44.0 | 37.0 | 19.0 | 1.9 |
| 3.5 | 6 | 11 | 15.0 | 85 | 55.0 | 39.0 | 42.0 | 19.0 | 2.2 |
| 3.8 | 6 | 11 | 30.0 | 17 | 34.0 | 59.0 | 27.0 | 14.0 | 1.9 |
| 3.8 | 6 | 11 | 30.0 | 85 | 38.0 | 58.0 | 26.0 | 16.0 | 1.6 |
| 3.8 | 3 | 11 | 1.0 | 17 | 37.0 | 56.0 | 31.0 | 13.0 | 2.4 |
| 3.9 | 3 | 11 | 1.0 | 85 | 57.0 | 37.0 | 48.0 | 15.0 | 3.2 |
| 2.9 | 3 | 11 | 15.0 | 17 | 28.0 | 71.0 | 17.0 | 12.0 | 1.4 |
| 3.1 | 3 | 11 | 15.0 | 85 | 34.0 | 65.0 | 23.0 | 12.0 | 1.9 |
| 3.0 | 3 | 11 | 30.0 | 17 | 25.0 | 76.0 | 14.0 | 10.0 | 1.4 |
| 3.3 | 3 | 11 | 30.0 | 85 | 32.0 | 71.0 | 18.0 | 11.0 | 1.6 |
| 4.0 | 3 | 5.5 | 15.5 | 85 | 34.0 | 61.0 | 27.0 | 12.0 | 2.2 |
| 3.5 | 3 | 1.4 | 15.5 | 17 | 28.0 | 73.0 | 17.0 | 10.0 | 1.7 |
| 3.6 | 3 | 1.4 | 15.5 | 85 | 30 0 | 69.0 | 19.0 | 12.0 | 1.6 |

rate, with a series of complex reactions occurring. Acetylene and methane were the major gaseous products. A yellow hydrocarbon solid was formed on the walls within the discharge zone. Minor gaseous reaction products were concentrated by use of a liquid nitrogen trap placed downstream from the reaction zone. These products were higher molecular weight hydrocarbons including ethane, propyne and *l*-pentane. The conversion efficiency of hydrogen to hydrocarbon product, both gaseous and solid, under these conditions was ca. 10 per cent.

3.2 *Oxygen discharge*

A rapid and extensive reaction occurred between the species produced in an oxygen discharge and carbon located downstream (oxygen pressure ca. 0.04 torr, linear flow rate ca. 180 cm sec $^{-1}$). The extent of reaction and concentration of gaseous products as a function of the distance of the graphitized carbon rod from the discharge, the dimensions of the sample, and the power input are summarized in Table 1.

In the absence of carbon, ca. 10 per cent of the oxygen was consumed. It was accounted for by observed equimolar amounts of CO and $CO_2$ as indicated by the cross-hatched area in Fig. 1. Contamination by stopcock grease is a likely source of carbon. However, a far more extensive reaction occurred when carbon was deliberately added to the system.

The extent of reaction of oxygen sharply decreased with increasing distance between the carbon rod and the discharge. This effect is shown in Fig. 1 for the 6 mm dia., 11 cm long rod. Power level also affected the extent of reaction, as is shown in Fig. 1. The difference in the extent of reaction as produced by 17 and 85 W output was more pronounced at short distances.

An eightfold change in the length of the 3 mm dia. carbon rod positioned 15.5 cm from the discharge did not significantly alter the per cent oxygen reacted, as shown in Table 1. However, the extent of reaction was very dependent upon the diameter of the rod in the gas stream, it being markedly increased when the rod diameter was increased from 3 to 6 mm.

The product CO–$CO_2$ ratio varied widely with experimental conditions used. In particular, the ratio changed widely with percentage of oxygen reacted, as shown in Fig. 2.

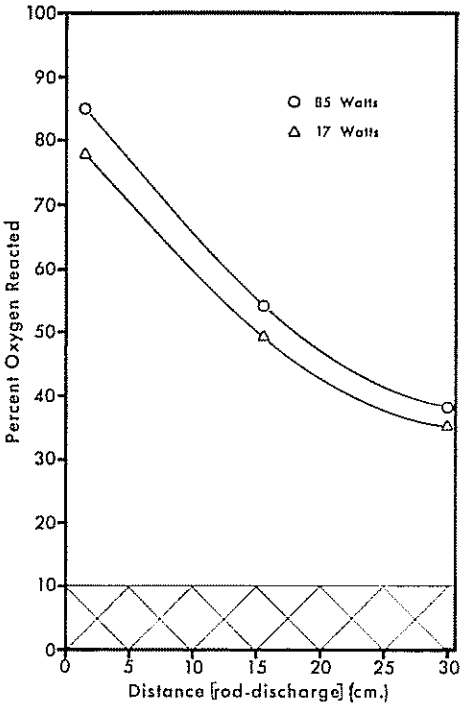


FIG. 1. Characterization of reaction of graphitized carbon rod with oxygen discharge. Effect of distance between discharge and sample and discharge power on oxygen consumed.

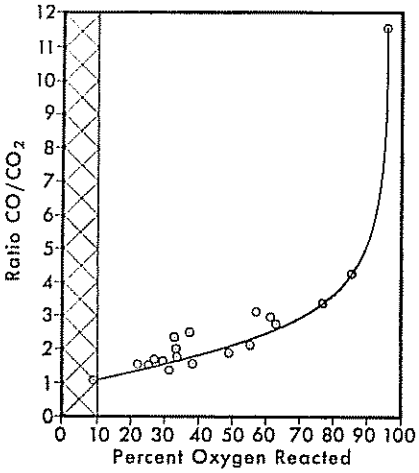


FIG. 2. Characterization of reaction of graphitized carbon rod with oxygen discharge. Effect of amount of oxygen reacted on product CO–$CO_2$ ratio.

3.3 *Water discharge*

In the absence of carbon, 48 per cent of the water was recovered from a water discharge (water pressure ca. 0.25 torr), the remainder appearing as molecular hydrogen and oxygen. If a carbon sample was placed outside the discharge, hydrogen and carbon monoxide were the major products. The extent of reaction and percentage of gaseous products are given in Table 2 for the case of a carbon rod 6 mm dia. and 11 cm long. It is seen that the product analysis changes with the distance between the carbon rod and discharge zone.

TABLE 2. CHARACTERIZATION OF REACTION OF CARBON WITH A WATER DISCHARGE

| Water pressure (torr) | Distance rod from discharge (cm) | Water reacted (%) | Mole per cent in product | | | | |
|---|---|---|---|---|---|---|---|
| | | | $H_2O$ | $H_2$ | CO | $CO_2$ | $O_2$ |
| ~ 0.25 | no rod | 52 | 38.0 | 41.0 | — | — | 21.0 |
| ~ 0.25 | 0.0 | 66 | 22.0 | 43.0 | 28.0 | 3.8 | 3.2 |
| ~ 0.25 | 5.7 | 57 | 30.0 | 41.0 | 16.0 | 3.0 | 10.0 |

3.4 *Hydrogen–carbon monoxide*

Very little rearrangement occurred when the mixture (pressure ca. 1 torr) was passed through the discharge; 98 per cent of the mixture was recovered along with small amounts of acetylene, methane, and a yellow solid similar to that obtained when carbon was placed in a hydrogen discharge.

## 4. DISCUSSION

4.1 *Hydrogen discharge*

In a hydrogen discharge in addition to hydrogen atoms, there are atomic ions and electrons.[7] Recombination of ionic species outside the discharge would be rapid and thus downstream from the discharge, only hydrogen atoms and molecules are present in any significant amounts. It is well established that hydrogen atoms can be present at considerable distances downstream from a discharge.[8–11] The rate of decay of the hydrogen atom concentration varies considerably depending on wall pretreatment, pressure, flow rate and water content of the hydrogen.

The observed recombination of hydrogen atoms on Pt also indicated a significant concentration of hydrogen atoms downstream from the discharge in the present work. It is concluded that hydrogen atoms do not react at an appreciable rate with carbon at room temperature. SHAHIN[12] has recently reached a similar conclusion.

WISE[13] has reported reaction between thin carbon films and hydrogen atoms. The temperature of the carbon films used in WISE's experiments was in the range of 200–300°C. Using a very sensitive mass spectrometer, only small amounts of hydrocarbons were detected. Thus, even at elevated temperatures, the rate of reaction between hydrogen atoms and carbon was very slow; the majority of the collisions of hydrogen atoms with the carbon surface resulted in recombination rather than reaction.

BLACKWOOD and MCTAGGART[4] reported that hydrogen atoms react with carbonized wood to produce methane, but the extent of the reaction is not indicated. The lower frequency used ($R_f$) could produce a discharge which enveloped the carbon sample. The reaction could then occur via ionic species. The explanation does not appear to lie with their use of a more reactive carbon, since preliminary research by us has shown that high surface are a carbon blacks and coals also react to a negligible extent with hydrogen atoms at room temperature.

A series of complex reactions occurs when carbon is placed directly in a hydrogen discharge. Although the steps in the reactions are uncertain, the transport of carbon from the solid to the vapor phase appears likely. This process might take place by bombardment of the carbon by energetic ionic species present in the discharge. The observed products could then result from the reaction and recombination of gaseous species. Spectral evidence obtained in this laboratory from the re-

arrangement of pure hydrocarbons in a microwave discharge indicates that CH is a possible intermediate.[14]

### 4.2 *Oxygen discharge*

In considering the results of the reaction of carbon with the active species from an oxygen discharge, the findings that the percentage oxygen reacted decreased with increasing distance of the carbon from the discharge and that the CO–$CO_2$ product ratio varied over wide limits should primarily be taken into account.

The observed decrease in the percentage oxygen reacted with increase in distance between the carbon rod and discharge (Fig. 1) is as expected. It has been shown[15] that the disappearance of oxygen atoms (to produce $O_2$) down a quartz tube from a microwave discharge is first order—or that the concentration decays exponentially with distance from the discharge. If the main oxygen-consuming reaction (that is, withdrawing oxygen from the system so that it cannot return to $O_2$ in the product) is $C + O \rightarrow CO$, then it is apparent that the amount of oxygen consumed will decrease as the carbon is placed farther downstream from the discharge.

It has been shown[15] that because of the reaction $O + O_2 + M \rightarrow O_3 + M$, ozone is also present downstream from an oxygen discharge. However, it is concluded from this work that the reaction of carbon with ozone at room temperature is negligible. If ozone were an active species, the reaction, $C + O_3 \rightarrow CO + O_2$, would appear to be the most probable, with equal amounts of $O_2$ and CO being produced. However, as indicated in Table 1, only small amounts of molecular oxygen were observed when carbon was present at small distances from the discharge. The conclusion that ozone is not the primary active species is substantiated further by the work of STREZNEWSKI and TURKEVICH.[2] These workers reported that no detectable reaction occurred between carbon films and ozone at room temperature at ozone pressures even greater than the initial oxygen pressures used in this work.

The marked variation in the CO–$CO_2$ ratio with amount of oxygen reacted should now be considered. There appear to be three possibilities for the production of $CO_2$: (i) that the homogeneous reaction, $CO + O + M \rightarrow CO_2 + M$, occurs; (ii) that CO reacts with chemisorbed oxygen atoms, $CO + (O) \rightarrow CO_2$; and, (iii) that excited oxygen molecules react directly with carbon, $C + O_2^{\bullet} \rightarrow CO_2$. On the basis of previous studies[15], it appears reasonable to assume, in this work, that the Pyrex tube downstream from the discharge is extensively covered with adsorbed oxygen atoms. In this case, upper limit calculations, assuming 100 per cent yield for each triple collision, show that at the low pressures operative in this study the homogeneous production of $CO_2$ occurs at a much slower rate than the heterogeneous production, as given by possibility (ii) above.

The second possibility is that the majority of the $CO_2$ comes from the reaction of CO with oxygen chemisorbed on the Pyrex surface downstream from the carbon sample. Under conditions of a fixed power level, oxygen pressure, and sample size, the CO–$CO_2$ ratio is experimentally found to decrease with distance of the carbon sample from the discharge. To the contrary, calculations show that the ratio should increase with distance, if the second possibility is primarily responsible for $CO_2$ production. It is concluded that the major reaction, under these conditions, producing $CO_2$ is $C + O_2^{\bullet} \rightarrow CO_2$. To be consistent with the variation in the CO–$CO_2$ product ratio, this would require that the concentration of $O_2^{\bullet}$ increased with increasing distance from the discharge over the range of sample location used in this study.

In previous studies[2] on the reaction of carbon with species from an oxygen discharge, no CO was found in the product. However, the study was conducted at a pressure of 1 torr, and a power level of 2070 W. Under these conditions, the homogeneous oxidation of CO would be much more rapid.

It is recalled that changing the diameter of the carbon rod had a substantial effect on the amount of reaction occurring; whereas, changing the length of the rod had only a minor effect. This result suggests ordered flow of the reactant gas in the annulus between the carbon rod and the tube wall, causing the reaction to occur principally at the end of the rod. Visual examination of the rod following reaction substantiated this conclusion.

### 4.3 *Water discharge*

The reaction of carbon with the products of a water discharge underscores the difference in reactivity of carbon with a hydrogen and oxygen

discharge. The water discharge conveniently serves as a simultaneous source of both hydrogen atoms and an active oxygen species. When the carbon sample is placed outside of the discharge zone, the hydrogen atoms recombine, as in a hydrogen discharge; and the active oxygen species reacts with carbon to produce primarily CO.

It is of interest to consider what the active oxygen species of a water discharge is. In this discharge, water would first be dissociated into H and OH. The presence of substantial amounts of $O_2$ in the product leads to the conclusion that OH was secondarily dissociated in the discharge to a significant extent to O and H. That is, the energetics of possible reactions for the production of oxygen atoms, or $O_2$ directly, outside of the discharge do not suggest rapid reaction rates. For example, the reaction $H + OH + M \rightarrow H_2 + O + M$ is estimated to be 7 kcal endothermic; the reaction $2OH + M \rightarrow O_2 + H_2 + M$ is estimated to be only 1 kcal. exothermic.

The production of oxygen atoms in the discharge is also consistent with the large production of CO when a carbon sample is placed downstream. That is, it appears, by elimination, that atomic oxygen must be the major active oxygen species. The reaction, $C + OH \rightarrow CO + H$, to produce CO is estimated to be endothermic by ca. 23 kcal; and, hence, would be expected to have a substantial activation energy and proceed at a low rate at room temperature.

From these results, it is seen that a reasonably good $CO$–$H_2$ synthesis gas mixture can be produced by reacting the products of a water discharge with carbon. Obviously it is desirable to locate the carbon very close to the discharge zone to decrease the amount of the active species which recombine to give $H_2O$ and $O_2$. Location of the carbon in the discharge zone would be expected to result in a further increase in $H_2$ and CO in the product gas. The desirability of this would have to be balanced against the microwave power consumed in heating of the carbon plus the production of some hydrocarbons. The latter effect, of course, could be an advantage depending upon what use was to be made of the synthesis gas mixture.

### 4.4 *Hydrogen–carbon monoxide discharge*

The fact that very little rearrangement occurred on passing a hydrogen–carbon monoxide mixture through the discharge dramatically illustrates the preferential reaction of oxygen atoms with carbon.

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