PLASMA POLYMERIZATION

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INTRODUCTION

Previous work with plasmas produced from hydrocarbons (1) demonstrated that both gaseous and solid plasma rearrangement products are produced. The distribution of these products depends upon the atomic hydrogen to carbon ratio of the reacting material. A limiting H/C ratio of approximately 1.6 was found for the solid. If the atomic H/C ratio of the starting material was greater than 1.6 both solid and gaseous products were formed, if the ratio was less than 1.6 only solid material was formed. With reacting gas ratios of less than 1.6 the solid would tend to have the same H/C ratio as the reacting gas.

The polymers produced by this process only depend upon the H/C ratio of the plasma and are independent of the molecular structure of the original reactants. With plasmas produced from single gases only a limited number of H/C ratios are available. However, by copolymerization of multicomponent mixtures solids of varying H/C ratio (max.=1.6) can be produced.

EXPERIMENTAL

Materials - Hydrogen (extra dry), acetylene (prepurified) and methane (CP) were obtained from the Matheson Co. The diacetylene was prepared according to the method described by Armitage, et al., (2) and purified by distillation.

Apparatus - The plasma generator consisted of a Raytheon* Diatherm unit (Model CMD 10) coupled to an Ophthos** cylindrical cavity. The frequency of the plasma generator was 2450 Mc. and the maximum output was 85 watts. The plasma reactions were carried out in a Pyrex bulb (vol.=150cc.) with a Vycor finger (OD=13mm).

Procedure - The experimental procedure consisted of filling the reaction bulbs with the reacting gas and analyzing the mixture mass spectrometrically before and after discharge; the H/C ratio of the solid produced is determined by making a material balance. The actual discharge takes place in the Vycor finger of the reaction bulb. The Vycor finger is positioned along the central axis of the cylindrical microwave cavity.

* Raytheon Co., Burlington, Mass.
** Ophthos Instrument Co., Rockville, Md.

RESULTS

Table I illustrates the relationship between the H/C ratio of the starting material and the H/C ratio of the solid produced.

Table I

DISCHARGE CHARACTERISTICS OF VARIOUS HYDROCARBONS

Mixture	H/C		Pressure, torr		Polymer Appearance
	Before Discharge	After Discharge	Before Discharge	After Discharge	
CH_4	4.00	1.60	3.49	3.86	Clear
C_4H_2-H_2	2.37	1.60	5.08	1.79	"
C_2H_2-H_2	1.59	1.48	5.40	0.53	"
C_2H_2-H_2	1.45	1.38	4.70	0.25	Very light brown
C_4H_2-CH_4	1.38	1.28	3.75	0.67	"
C_4H_2-CH_4	1.31	1.26	2.50	0.10	Light brown
C_4H_2-H_2	1.23	1.20	2.70	0.05	"
C_2H_2-H_2	1.20	1.20	4.10	0.02	"
C_4H_2-H_2	1.20	1.19	5.42	0.15	"
C_2H_2	1.00	1.00	5.02	0.03	Brown
C_2H_2	1.00	1.00	4.90	0.03	"
C_4H_2-CH_4	0.80	0.80	4.85	0.08	Dark brown
C_4H_2-H_2	0.80	0.80	5.32	0.02	"
C_4H_2	0.50	0.50	2.72	0.06	Very dark brown
C_4H_2	0.50	0.50	3.35	0.02	"

If the initial H/C ratio is greater than 1.6 the solid will have a limiting H/C ratio of 1.6 and the remainder of the hydrogen and carbon in the system will be in the gas phase. Table II gives the composition of the gases remaining after a discharge lasting 120 seconds for a plasma produced from methane (H/C=4) and one produced from a diacetylene-hydrogen mixture (H/C=2.37).

Table II

	CH_4		C_4H_2-H_2	
	Analysis, mole %			
	Before Discharge	After Discharge	Before Discharge	After Discharge
H_2	---	49	79	89
CH_4	100	50	--	3
C_2H_2	---	1	--	--
C_4H_2	---	--	21	8

With a H/C ratio of less than 1.6 most of the starting material will be incorporated in the solid, and the discharge will be extinguished when the pressure remaining in the reactor reaches the lower pressure limit of the plasma generator.

Table III gives the time elapsed before a discharge will be extinguished for a series of diacetylene-hydrogen mixtures of constant total pressure and varying H/C ratio.

Table III

Plasma Extinction Time for C_2H_4-H_2 Mixtures

Total Pressure, torr	Ratio	Discharge Time, sec.
2.0	1.22	15
2.0	1.41	22
2.0	1.53	31
2.0	1.66	> 120

DISCUSSION

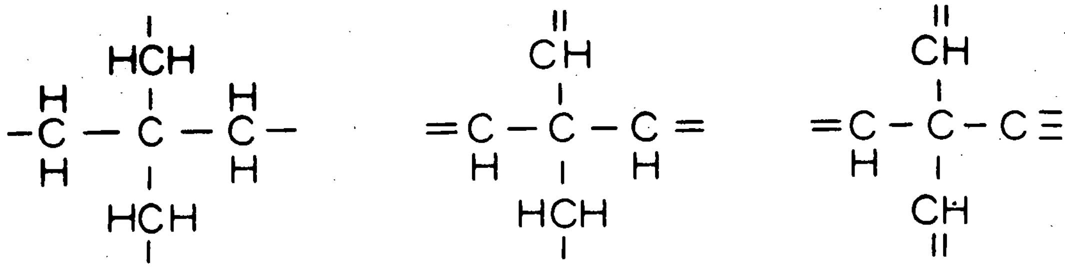
A hydrocarbon solid is one of the stable products formed by a hydrogen-carbon plasma. The maximum H/C ratio of this solid is approximately 1.6. This value cannot be exceeded even in cases where the H/C ratio of the plasma is greater than 1.6. The minimum H/C ratio of the solid is determined by the minimum H/C ratio of the hydrocarbon that is used for the plasma discharge, in this work the minimum H/C was 0.5 (diacetylene, C_4H_2). Table III illustrates that it is more difficult to produce solids as the H/C ratio approaches 1.6.

The physical appearance of the solids varied in a continuous manner from a clear, flexible film of H/C=1.6 to a very dark brown, brittle film of H/C=0.5. Infrared absorption analysis indicated no measureable aromatic structure even with a H/C ratio of 0.5. Absorption in the wave length regions 6.2 and 3.0-3.15 microns increased as the H/C ratio approached 0.5 indicating an increase in the degree of unsaturation. The decomposition products resulting from vacuum pyrolysis of the polymers were primarily hydrogen with a lesser amount of hydrocarbon gases ranging up to C_{10}. The majority of the C_4 to C_{10} hydrocarbons were highly branched compounds. No solvent was found for any of the polymers.

A possible structure for an insoluble, saturated aliphatic polymer with a H/C ratio of 1.6 is shown in Figure 1(a). This tetrahedral monomeric unit would form a three dimensional highly branched polymer; further hydrogenation would tend to destroy the polymeric structure. Since the polymers produced with H/C ratios varying from 0.5 to 1.6 seem to be part of a series, the structures shown in Figure 1(b) and 1(c) are possibilities of varying degrees of saturation of the basic monomer unit.

REFERENCES

1. F. J. Vastola and J. P. Wightman, J. Appl. Chem., in press.
2. J. B. Armitage, E. R. H. Jones, and N. C. Whiting, J. Chem. Soc., (1951), 44.



H/C = 1.6 (a) — H/C = 1.0 (b) — H/C = 0.6 (c)

MONOMER STRUCTURE FOR VARIOUS H/C RATIOS

FIGURE 1