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Mass-Spectrometric Investigation of the Reaction of Hydrogen with Graphite at 1900°–2400°K[*]

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An integral furnace mass spectrometer was used to directly observe the products of the reaction of hydrogen with graphite between 1880° and 2430°K at pressures up to 0.5 torr and with 80-msec contact times. Ions observed to *m/e* 140 indicate formation of an extensive high-molecular-weight hydrocarbon system consisting mainly of unsaturated, acyclic, nonaromatic compounds. Many of these compounds were formed in steady-state concentrations much greater than expected for equilibrium. A reaction mechanism involving addition and insertion reactions is discussed.

INTRODUCTION

Both predictions[1–3] and experiments[4–12] suggest that the high-temperature (1000°K and above) carbon–hydrogen system differs from the well-studied, extensive, lower-temperature hydrocarbon system. Radicals and unsaturated hydrocarbons that are reactive or unstable at ordinary temperatures are the predominant carbon–hydrogen molecules at high temperatures. Knowledge of the behavior of this high-temperature system is important because of the use of hydrocarbons as fuels and the use of graphite and carbides as refractory materials. Because carbon and hydrogen are major stellar components, work with this system should lead also to a better understanding of the universe and of paleochemistry.[10,13]

Studies of the high-temperature carbon–hydrogen system can be roughly divided into hot-graphite–hot-hydrogen (approach-to-equilibrium) and hot-graphite–cold-hydrogen (nonequilibrium) work. Experiments of the first group include integral furnace mass spectrometry,[8] carbon tube furnace,[6,9] and carbon arc studies.[2,7] Those of the second group involve the reaction of hydrogen or hydrocarbon gases with hot graphite filaments, rods, or pieces,[3,4,10–12] and with exploding graphite wires.[14,15] In all but the mass-spectrometric study,[8] the high-temperature reaction species are not directly observed but had to be inferred from analysis of quenched reaction products. Quench reactions of high-temperature molecules such as C and C_3 with hydrocarbon gases or condensed hydrocarbon matrices[16–31] also have been studied.

Several sets of theoretical predictions for the equilibrium high-temperature carbon–hydrogen system have been made but have not been verified in detail since attainment of equilibrium in this system, even at 2000°–3000°, is difficult. The most extensive set of predictions is that of Duff and Bauer[1] who consider

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[†] Recipient of Public Health Service Fellowships 1-F1-GM-29-815-01A1 and 5-F1-GM-29, 815-02 from the National Institute of General Medical Sciences, 1966–1968.

[1] R. E. Duff and S. H. Bauer, J. Chem. Phys. **36**, 1754 (1961).

[2] R. F. Baddour and J. L. Blanchet, Ind. Eng. Chem. Process Design Develop. **3**, 258 (1964).

[3] B. Lersmacher, H. Lydtin, W. F. Knippenberg, and A. W. Moore, Carbon **5**, 205 (1967).

[4] Z. Szabo, J. Am. Chem. Soc. **72**, 3497 (1950).

[5] L. C. Browning and P. H. Emmett, J. Am. Chem. Soc. **73**, 581 (1951).

[6] M. N. Plooster and T. B. Reed, J. Chem. Phys. **31**, 66 (1959).

[7] R. F. Baddour and J. M. Iwasyk, Ind. Eng. Chem. Process Design Develop. **1**, 169 (1962).

[8] W. A. Chupka, J. Berkowitz, D. J. Meschi, and H. A. Tasman, Advan. Mass. Spectrometry, Proc. Conf., 2nd, Oxford, 1961, 99, (1963).

[9] Z. V. Ievleva, Zh. Fiz. Khim. **38**, 2380 (1964).

[10] E. A. Gulbransen, K. F. Andrew, and F. A. Brassart, J. Electrochem. Soc. **112**, 49 (1965).

[11] E. A. Gulbransen, Nature **212**, 1420 (1966).

[12] J. T. Clarke and B. R. Fox, J. Chem. Phys. **46**, 827 (1967).

[13] M. O. Dayhoff, E. R. Lippincott, R. V. Eck, and G. Nagarajan, "Thermodynamic Equilibrium in Prebiological Atmospheres of C, H, O, N, P, S, and Cl," NASA SP-3040, Washington, D.C., 1967.

[14] C. W. Spangler, S. K. Lott, and M. J. Joncich, Chem. Commun. **1966**, 842.

[15] C. W. Spangler, S. K. Lott, and M. J. Joncich, Electrochem. Tech. **5**, 214 (1967).

[16] C. MacKay and R. Wolfgang, J. Am. Chem. Soc. **83**, 2399 (1961).

[17] C. MacKay, J. Nicholas, and R. Wolfgang, J. Am. Chem. Soc. **89**, 5758 (1967).

[18] C. MacKay and R. Wolgang, Science **148**, 899 (1965).

[19] M. Marshall, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **86**, 4741 (1964).

[20] J. Dubrin, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **86**, 4747 (1964).

[21] J. Dubrin, C. MacKay, and R. Wolfgang, J. Chem. Phys. **41**, 3267 (1964).

[22] J. E. Nicholas, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **87**, 3008 (1965).

[23] T. Rose, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **88**, 1064 (1966).

[24] J. Nicholas, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **88**, 1610 (1966).

[25] J. Nicholas, C. MacKay, and R. Wolfgang, Tetrahedron **22**, 2967 (1966).

[26] T. Rose, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc. **89**, 1529 (1967).

[27] P. S. Skell and L. D. Wescott, Jr., J. Am. Chem. Soc. **85**, 1023 (1963).

[28] P. S. Skell and R. R. Engel, J. Am. Chem. Soc. **87**, 1135 (1965).

[29] P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, J. Am. Chem. Soc. **87**, 2829 (1965).

[30] R. R. Engel and P. S. Skell, J. Am. Chem. Soc. **87**, 4663 (1965).

[31] J. L. Sprung, S. Winstein, and W. F. Libby, J. Am. Chem. Soc. **87**, 1812 (1965).

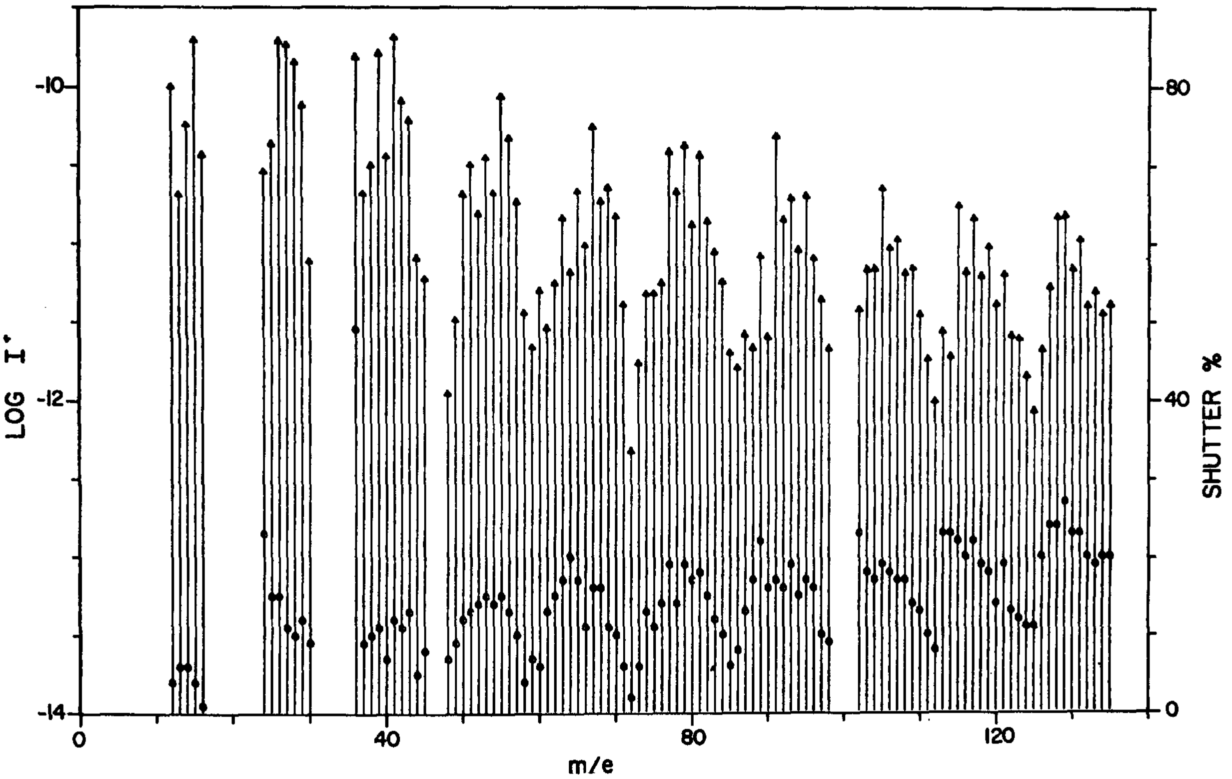

FIG. 1. Molecular-beam mass spectrum of products from the reaction of 3% methane/97% hydrogen with ATJ graphite at 2360°K. The left-hand axis is the logarithm of the ion intensity (triangles), and the right-hand axis is the percentage shutter effect[33] (circles). Mass peaks 98–102 are missing because of the difficulty in resolving the low-intensity hydrocarbon peaks from those of doubly charged mercury. Mass peak 45 probably corresponds to $^{13}CO_2$. $I(H^+)$ and $I(H_2^+)$ are 4×10^{-10} and 4×10^{-9} A, respectively.

57 hydrocarbon species; a smaller set of species is used by Baddour and Blanchet.[2] Qualitative experimental agreement has been obtained by Lersmacher *et al.*[3] for another set of predictions. Theoretical predictions for the carbon–hydrogen–oxygen system also are available.[13]

In this paper is reported the direct observation by the molecular-beam mass-spectrometric technique of hydrocarbon species formed by the reaction of hydrogen with graphite in a flow reactor with an 80-msec contact time. Reactions were observed at temperatures between 1880° and 2430°K and at hydrogen pressures up to 0.5 torr.

EXPERIMENTAL

A Nuclide Analysis Associates 12-in. −60° sector HT mass spectrometer[32–34] with an inlet system[35] modified to give a constant, low hydrogen pressure was used.

Matheson prepurified-grade hydrogen or a 3 mole % methane/0.03% ethane/97% hydrogen mixture was passed over 4-mm-cube chunks of ATJ (high-purity, density 1.73) graphite or four-mesh Norton Company high-boron-content-grade boron carbide, either of which was loosely packed to fill thee-quarters of the crucible. Pieces of sample were placed over the inlet to the reactor so that the hydrogen or any products formed in a backflow from the cell would undergo numerous wall collisions before effusing from the 0.037-cm-diam orifice. Electron bombardment was used for heating; the temperature was read at radiation holes at the top and bottom of the crucible by means of an optical pyrometer; an emissivity correction of 0.85 has been made for the grayness of the holes and attenuation by the intervening window. A 100°–200° temperature gradient, caused in large part by the gas inlet stem, was normally observed over the crucible, and accordingly the place of observation is given with the reported temperatures.

A movable beam defining slit ("shutter"), located between the crucible orifice and the ion source permitted differentiation of species originating from the crucible, the crucible lip, the radiation shields, and the residual background gases.[32–34]

The ion-source conditions typically were: emission

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[32] M. G. Inghram and J. Drowart, *High Temperature Technology* (McGraw-Hill Book Co., New York, 1960), p. 219; W. A. Chupka and M. G. Inghram, J. Phys. Chem. **59**, 100 (1955).

[33] F. E. Stafford, G. A. Pressley, Jr., and A. B. Baylis, Advan. Chem. Ser. **72**, 137 (1968).

[34] A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, J. Am. Chem. Soc. **88**, 2428 (1966).

[35] S. J. Steck, G. A. Pressley, Jr., and F. E. Stafford, J. Phys. Chem. (to be published).

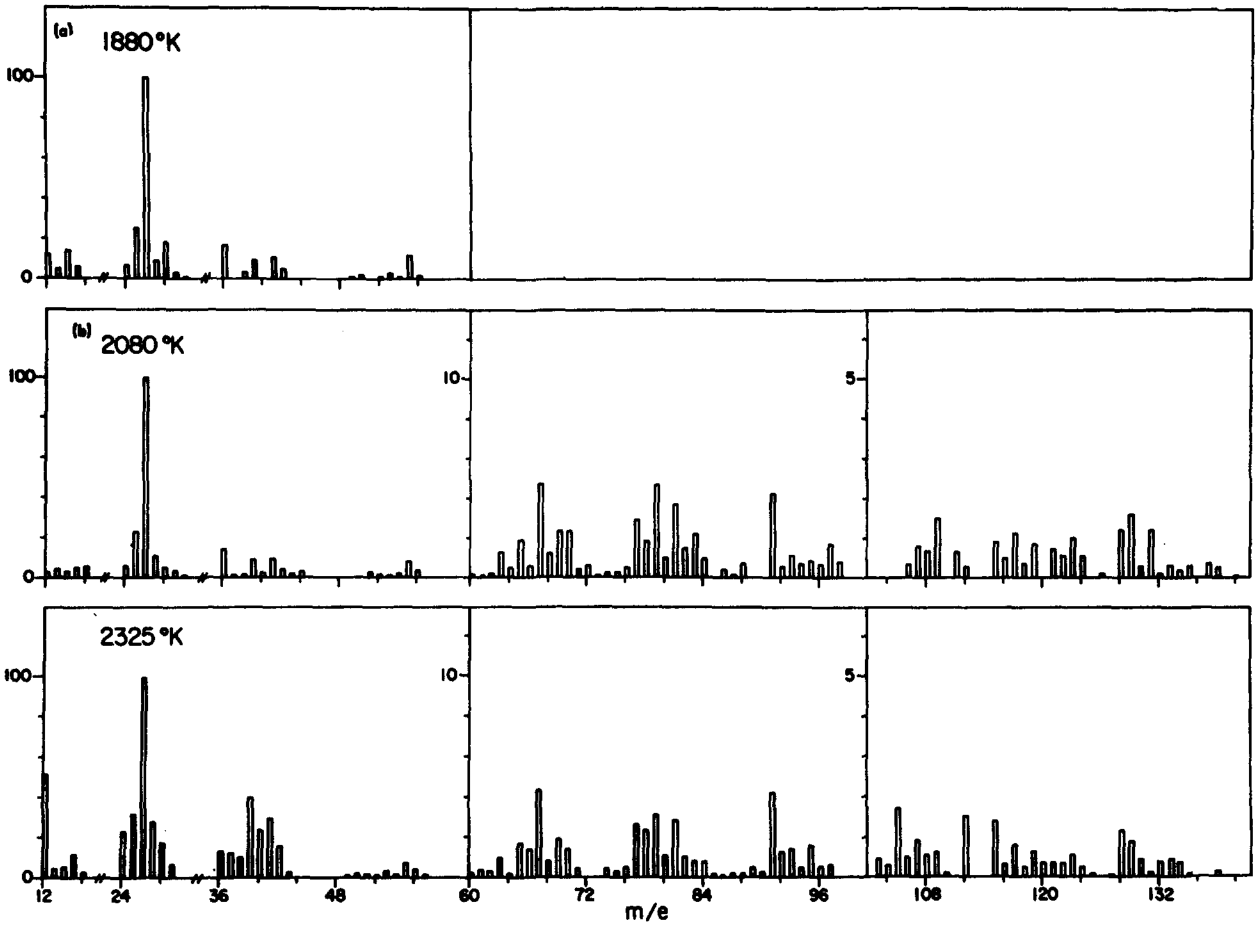

FIG. 2. Molecular-beam mass spectrum of products of the reaction of 0.03–0.05 torr hydrogen with ATJ graphite. Top spectrum, Run 671202-1 (1805°K, bottom radiation hole; 1880°K, average); high-molecular-weight ions were of low intensity and could not be measured. Middle spectrum, Run 671202-2 (2005°K, bottom radiation hole; 2081°K, average). Bottom spectrum, Run 671202-3 (2212°K, bottom radiation hole; 2315°K average). Spectra were taken in order of increasing temperature. For solid bars, multiply intensities by 10.

current, 1.2 mA (which corresponds to a trap current of about 10^{-5} A); ionizing electron voltage, 70 eV; and accelerating voltage, 4 kV. Appearance-potential curves were automatically plotted on an $X-Y$ recorder[36] and were analyzed by the vanishing current technique[37] with argon as the calibrant.

Ions were detected with both a 50% transmission grid and a 20-stage secondary electron multiplier operated at 2.5 kV. Spectra presented in the various figures and tables, however, are not corrected for multiplier gain because the intensities of many of the ions were too small to be detected by the grid.

DATA

Spectra

Mass peaks 1–140, the latter being an arbitrary stopping point because of time limitations, were examined at temperatures between 1880° and 2430°C and at hydrogen pressures up to 0.5 torr in the crucible reactor. Higher mass ions were observed, but not studied. Ions were identified on the basis of mass defect, isotope ratios, and shutter percents.[38] Only ion intensities due to molecular-beam ("shutterable") species are discussed.

The C_2^- or other negative ions that have been identified previously[39] in the vapor phase above carbon and any charged products formed from them could not be detected without major modification of the apparatus.

Before hydrogen was admitted into the reactor, many hydrocarbon ion peaks were present as a ubiquitous background. With ATJ graphite samples above 1900°C, the only shutterable ions, however, were m/e 12 (C^+), m/e 24 (C_2^+), and m/e 36 (C_3^+); boron carbide

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[36] R. J. Loyd and F. E. Stafford, Advan. Chem. Ser. **72**, 127 (1968).

[37] R. W. Kiser, *Introduction to Mass Spectrometry and Its Applications* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965), pp. 166ff.

[38] "Shutter percent" is the ratio of the molecular-beam intensity to the total ion intensity at a given mass peak. Argon, for example, would show about a 4% shutter effect at these temperatures. Ions from a reactive species, one that is rapidly pumped by collisions with the vacuum chamber walls, would have a 100% shutter effect.

[39] R. E. Honig, J. Chem. Phys. **22**, 126 (1954).

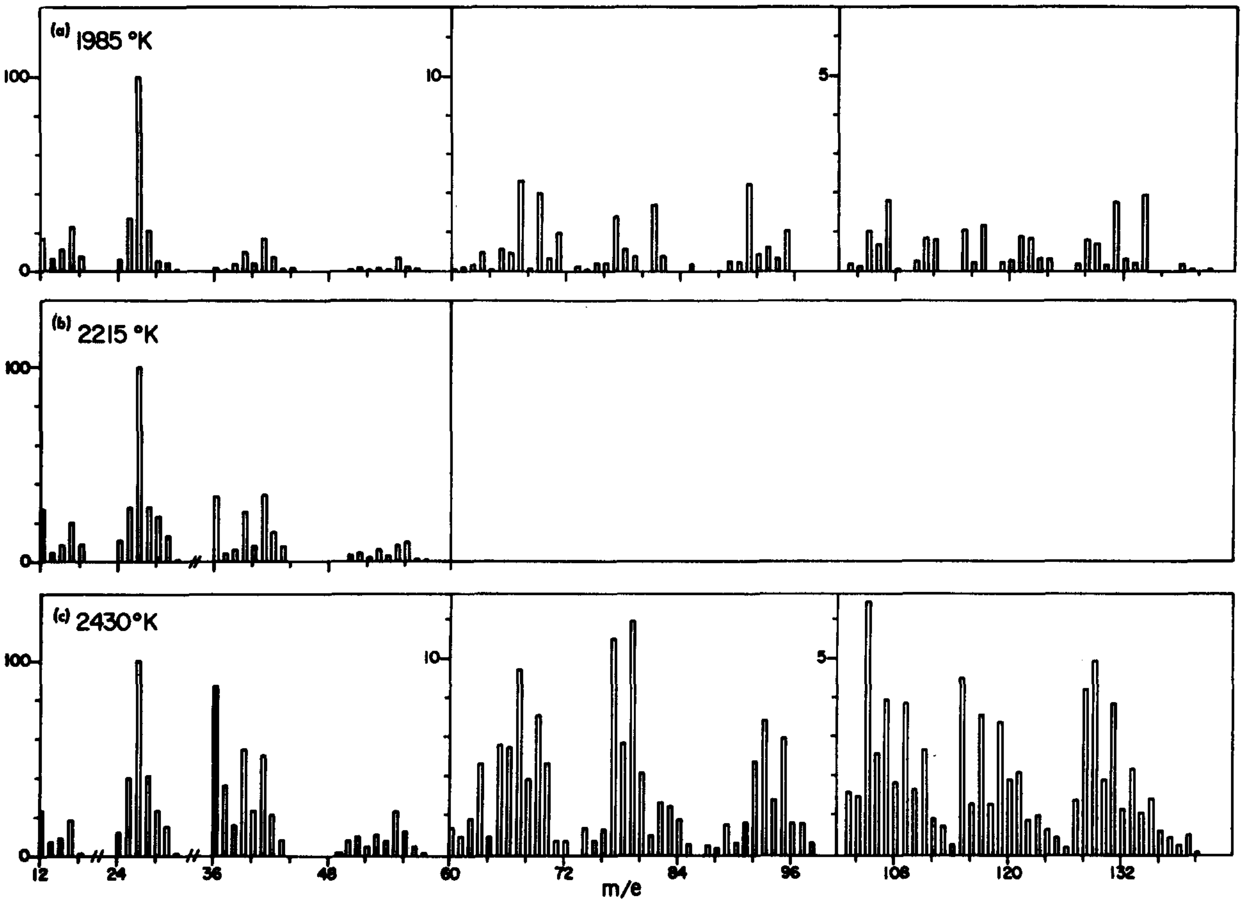

Fig. 3. Molecular-beam mass spectrum of products of the reaction of 0.03–0.05 torr hydrogen with ATJ graphite. Top spectrum, Run 671205-1 (1900°K bottom radiation hole; 1985°K, average). Middle spectrum, Run 671206-2 (2110°K, bottom radiation hole; 2215°K, average); high-molecular-weight ions were not measured because heating filaments burned out. Bottom spectrum, Run 671206-1 (2315°K, bottom radiation hole; 2430°K, average). Spectra were taken in the order 67105-1, 671206-1, 67106-2. For solid bars, multiply intensities by 10.

samples sometimes gave, in addition, shutterable ion intensities at *m/e* 25 (C_2H^+) and *m/e* 26 ($C_2H_2^+$). Hydrocarbon species arising from the crucible lip were sometimes observed while the crucible was degassing.[40]

After hydrogen was introduced into the crucible, all possible hydrocarbon ions through *m/e* 140 were identified as molecular-beam species, indicating formation of hydrocarbons in the reactor. The same hydrocarbon ions were observed with either graphite or boron carbide samples. Relative intensities of the hydrocarbon ions arising from the graphite or the boron carbide samples appeared comparable when experimental differences of machine sensitivity, temperature, and pressure were considered. Figure 1, for instance, gives a logarithmic plot of the shutterable hydrocarbon ion intensity obtained for the reaction of 97% hydrogen–3% methane with ATJ graphite at 2360°K. Ion current (triangles) is shown on the left-hand axis as amperes of net multiplier output; actual ion currents are 10^5–10^6 smaller and often correspond to ions per second. Shutter percents[38] (circles) are shown on the right-hand axis. Mass peaks 98–102 are missing because of the difficulty in resolving the low-intensity hydrocarbon peaks from those of doubly charged mercury. Intensities of *m/e* 1 and 2, which are too intense to be given in Fig. 1, are 4×10^{-10} and 4×10^{-9} A, respectively; corresponding shutter effects[38] for these ions are 50% and 4%. Additional spectra with linear intensity scales are given in Figs. 2–5. Measurement of each full spectrum shown required 12–15 h. The groups of three spectra in Figs. 2 and 4 were measured consecutively without breaks between them, without cooling down the reactor, and without changing instrument sensitivity; the spectra in each of these figures are, therefore, most directly comparable amongst themselves. Hydrogen pressures for the spectra in Fig. 4, in particlar, are known relative to one another from $I(H_2^+)$ measurements; from one figure to another however, the absolute pressures of hydrogen and/or other species are uncertain by a factor of 2–3.

Two general trends were observed in all the spectra measured and are shown in Fig. 1: (1) a slow decrease in ion intensity with increasing molecular weight and (2) an increase in shutter percent[38] from about 5% to about 25% with increasing molecular weight. As

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[40] *Nuclear Graphite*, R. E. Nightengale, Ed. (Academic Press Inc., New York, 1962), pp. 22–49, 435.

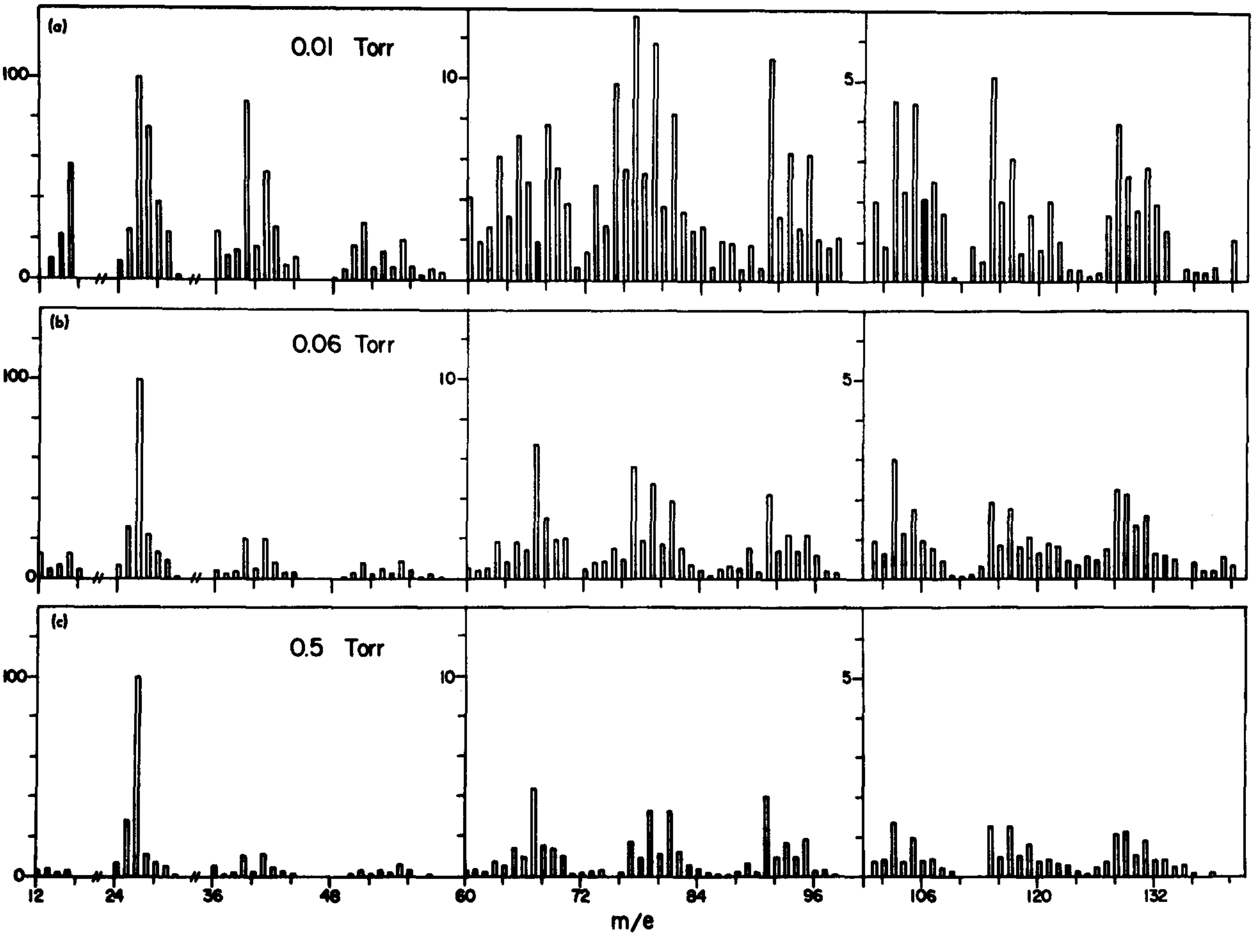

FIG. 4. Molecular-beam mass spectrum of products of the reaction of hydrogen with ATJ graphite (2225°K, bottom radiation hole). Top spectrum, Run 670405-1, 0.01 torr hydrogen. Middle spectrum, Run 560405-2, 0.06 torr hydrogen. Bottom spectrum, Run 670405-3, 0.5 torr hydrogen. Spectra were taken in the order of increasing hydrogen pressure. For solid bars, multiply intensities by 10.

expected, *m/e* 36, arising in large part from C_3 neutral, has a large shutter effect. The spectrum consists of a series of envelopes that correspond to the different possible numbers of carbon atoms in the ions; the largest ion intensities appear in the center of the envelopes.

In each of the hydrocarbon envelopes, one or two ions are particularly intense. Comparison[41] of numerous hydrocarbon mass spectra has indicated that compounds with different degrees of unsaturation give rise to different characteristic ions normally differing from one another in increments of two mass units (H_2) as do the neutral progenitors. Some of these ions are listed in Table I. It seems probable that this increment difference exists also at higher temperatures even though fragmentation patterns are known to change with temperature. In the observed spectra, therefore, the most intense ions become increasingly more unsaturated with increasing numbers of carbons; in general, ion peaks characteristic of alkanes are least abundant.

Temperature

The effect of increasing temperature from 1880°–2430°K is shown by the six mass spectra in Figs. 2 and 3; hydrogen pressures used for all spectra are nominally the same (~0.03–~0.06 torr). Absolute intensity of the base peak, *m/e* 26 ($C_2H_2^+$) increased by factors of 8 and 4.5 in the 445° intervals covered in Figs. 2 and 3, respectively. High-molecular-weight species, rather than disappearing with increasing temperature as predicted,[1–3] increase in absolute intensity and also relative to *m/e* 26, as shown clearly in Fig. 3. This large increase in hydrocarbon content of the vapor seems to be related to the corresponding increase of C, C_2, and/or C_3 partial pressures by $\sim 10^4$ over the temperature interval. A trend toward increased unsaturation of the ions also is marginally observable.

Hydrogen Pressure

The effect of increasing hydrogen pressure by a factor of ~50 is shown by the mass spectra in Fig. 4.

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[41] F. W. McLafferty, *Interpretation of Mass Spectra* (W. A. Benjamin, Inc., New York, 1967).

Data given in Table II for the reference peak, *m/e* 26, believed to be due primarily to acetylene, show sensibly a first-power hydrogen dependence; that for *m/e* 1, believed to be due primarily to the hydrogen atom, shows the expected half-power dependence. Although the absolute intensity of other hydrocarbon ions increase with pressure, the increase is less than a first-power dependence as shown by the decrease in abundance of these ions compared to *m/e* 26 in Fig. 4; the increases in intensity relative to *m/e* 26 of 50, $(50)^2$, ···, expected for species containing 4, 6, ···, hydrogens, clearly, are not observed. A slight, but reproducible trend toward increasing saturation is observed with increased hydrogen pressure.

Added Methane

The effect of an added hydrocarbon (3 mole % methane/97% hydrogen) is shown by comparison of the mass spectrum in Fig. 5 with those in Figs. 2(c) and 4(a) and 4(b). Reactant pressure for Fig. 5 is approximately equal to that for Fig. 2(c) and intermediate between those in Figs. 4(a) and 4(b); the temperature of the methane run was approximately 35° higher than that for 2(c) and 60°–80° higher than that for 4(a) and 4(b). In Fig. 5, the larger relative amounts of *m/e* 16 (CH_4^+) and *m/e* 15 indicate that methane has not completely pyrolyzed. Moreover, intensities of *m/e* 28 ($C_2H_4^+$), *m/e* 30, and higher-molecular-weight hydrocarbon ions have increased conspicuously. (Note that the solid bars should be increased in height tenfold.) These increased intensities seem to correlate with increased carbon content of the vapor, as do the effects of increasing temperature. Other changes also are reproducible; addition of methane appears to result in increased saturation of species with three or more carbons. In particular, the intensity of *m/e* 41 has increased relative to *m/e* 39. Both of these ions have increased relative to the $C_2H_x^+$ ion group.

TABLE I. Characteristic ion fragment peaks for hydrocarbons.[a]

Alkanes	Alkenes cycloalkanes	Alkynes dienes, etc.	Aromatics
15			
29	27		
43	41	39	39
57	55	53	50, 51, 52
71	69	67	63, 64, 65
85	83	81	75, 76, 77, 79
99	97	95	91
113	111	109	
127	125	123	

[a] See, for instance, Ref. 41.

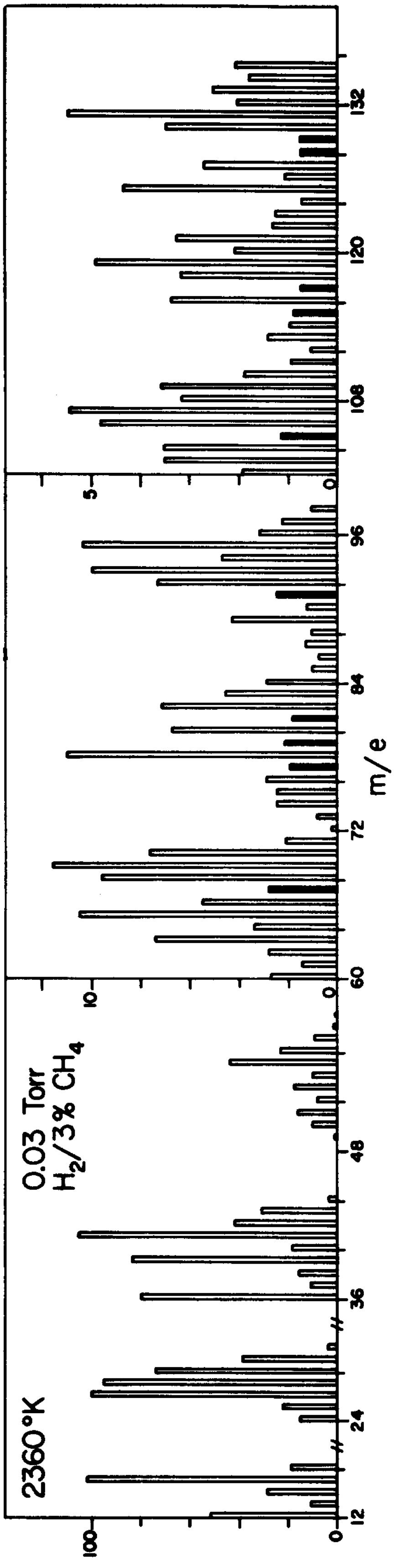

FIG. 5. Molecular-beam mass spectrum for the reaction of 0.03 torr 3% methane–97% hydrogen mixture with ATJ graphite (2295°K, bottom radiation hole; 2360°K, average). For solid bars, multiply intensities by 10.

TABLE II. Changes in the intensities[a] of H^+, and $C_2H_2^+$ relative to that of H_2^+.[b]

$I(H_2^+)\times10^9$	$I(H^+)\times10^{10}$	$I(C_2H_2^+)\times10^{11}$
3.7	1.26	4.1
36	4.1	21.
177	7.9	140

[a] In amperes.

[b] Run 670405; 0.01, 0.06, and 0.5 torr nominal pressures, see Fig. 4. $I(H_2^+)$ and $I(H^+)$ are corrected for neither cross section nor secondary electron multiplier gain, Ref. 35.

INTERPRETATION OF RESULTS

Identification of Neutral Progenitors

The spectra in Figs. 1–5 are too complex for unambiguous assignment of most of the neutral progenitors. Variation of fragmentation patterns of hydrocarbons with temperature add additional uncertainties. Some inferences, however, can be made and are partially confirmed by appearance potentials and/or large percentage shutter effects.[38]

The peaks at *m/e* 16, 30, 44, and 58 indicate the presence of methane, ethane, propane, and butane; the only other source of these ions is through rearrangement processes. Relatively large intensities at *m/e* 28 ($C_2H_4^+$), the parent and most intense peak in the ethylene spectrum, suggest the presence of ethylene. Similarly, the large intensity and consistently large shutter effect at *m/e* 26 ($C_2H_2^+$) strongly indicate acetylene. Mass peak 78 is the parent and most intense peak in the benzene spectrum; since *m/e* 78 is only slightly larger than expected on the basis of the surrounding ions, benzene appears to be present in small quantities. Mass peak 128, the principal and most intense peak of naphthalene, is characteristic also of some heavier aromatics. This ion is generally larger than the envelope of the surrounding even mass peaks and is indicative of naphthalene and/or heavier aromatics. The presence of small quantities of aromatics is suggested also by the intensity of *m/e* 91 ($C_7H_7^+$, the tropylium ion) which is normally 2–4 times larger than the band contour of neighboring ions. Because only small quantities of aromatics are indicated by the high-molecular-weight ions, lower-molecular-weight ions characteristic of aromatics may result from unsaturated molecules instead; *m/e* 50 and 52, which are relatively intense for highly unsaturated, even mass ions, may arise partially as the intense molecular ions of diacetylene and vinylacetylene. These compounds have been identified in other high-temperature studies.[6,7]

Table III gives the appearance potentials (A.P.'s) obtained for some of the more intense ions at ~2050°C. Each entry represents at least two and often three separate measurements of curves drawn simultaneously as ion intensity vs time (decreasing voltage) on the instrument recorder and as intensity vs voltage on two auxilary *X–Y* recorders. Where two values are recorded for an ion, they are the results of experiments done several months apart. The precision is ±0.2 eV for many of the determinations but the high temperatures of the experiment result in an expected accuracy of about ±1 eV. Use of the vanishing current method of analysis may be questionable, particularly for the fragment ions,[37] but because of the large number of suspected contributors to many of the ions, this method appears to be the best way to detect radicals and molecular ions.

Because of the small ion intensities available, only total ion intensities—molecular beam plus background—were used in the ionization efficiency curves. This posed few problems where free radicals and unsaturated species were to be identified because the background ions arose from fragmentation processes having relatively high appearance potentials. In all cases, the percentage shutter effects were measured 1 eV above the appearance potential to verify the continued presence of a molecular-beam species.

Possible neutral progenitors listed by Field and Franklin[42] as having processes with an appearance potential within 1 eV of the observed one are given in column 3 with the appearance potential in column 4 of Table III.

Appearance potentials for *m/e* 15 (CH_3^+) and 29 ($C_2H_5^+$) were too low for most fragmentation processes (see Table III, columns 3 and 4), but were not low enough to assign the radicals CH_3 and C_2H_5 as the neutral progenitors without ambiguity. Very large shutter effects[38] (75%–100%) obtained for both 1 V above the appearance potentials indicate that the free radicals are indeed among the respective neutral progenitors. Previous experimental work with free radicals has shown that the ionization efficiency curves contain several breaks,[43] which, unless high sensitivity is available, lead to high values of the deduced A.P.'s. This suggests that other radicals such as CH_2, C_2H, C_2H_3, and C_3H could be present in spite of the relatively high A.P.'s observed.

The A.P.'s given in Table III for $C_2H_2^+$ and $C_2H_4^+$ show that acetylene and ethylene are among the unsaturated hydrocarbon reaction products. Relatively low A.P.'s (compared to those of neighboring ions) indicate other unsaturated products corresponding to the formulas C_3H_4, C_3H_6, C_4H_6, C_4H_8, C_5H_6, C_5H_8, C_6H_6, C_6H_8, C_6H_{10}, and C_6H_{12}. Because of the large numbers of possible isomers for many of these formulas, assignment of the products is more difficult; possibilities for some of them are allene and/or propyne, cyclopropane and/or propene, (1-) butyne, (1-) butene, and benzene.

Appearance potentials indicate also the presence of

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[42] F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957).

[43] C. E. Melton and W. H. Hamill, J. Chem. Phys. **41**, 3464 (1964).

TABLE III. Appearance potentials[a] for some hydrocarbon ions observed in the reaction of hydrogen with ATJ graphite.

Ion	Observed A.P.	Possible progenitor	A.P. from progenitor[b]
C^+	12.2±0.2	C	11.26
CH^+	16.9±0.2	CH_2	17.1
		CH_3	16.2
CH_2^+	15.3±0.2	CH_3	15.29
		CH_4	15.6[c]
CH_3^+	11.03±0.09	CH_3	9.9[c]
		CH_4	14.3[c]
C_2^+	12.2±0.4	C_2	11.5
C_2H^+	13.2±0.5	C_2H_2	17.9
$C_2H_2^+$	11.3±0.3	C_2H_2	11.41
$C_2H_3^+$	12.9±0.5	C_2H_4	14.0[c]
		C_3H_6	13.7[c]
		cyclo-C_3H_6	13.37
		1-C_4H_8	13.6
		cis-2-C_4H_8	13.8
		trans-2-C_4H_8	14.0
		cyclo-C_5H_8	13.0
$C_2H_4^+$	10.8±0.3	C_2H_4	10.51
		n-C_4H_{10}	11.4[c]
$C_2H_5^+$	9.88±0.14	C_2H_5	8.72[c]
		C_2H_6	12.8[c]
$C_2H_6^+$	12.2±0.2	C_2H_6	11.6[c]
C_3^+	11.97±0.10	C_3	12.6[d]
	11.93±0.11	*cyclo*-C_3H_6	12.4
$C_3H_2^+$	15.0±0.5	C_3H_6	15.1
		$CH_2{=}C{=}CH_2$	14.2
		$CH_3C{\equiv}CH$	14.0
		cyclo-C_5H_6	15.5
$C_3H_3^+$	12.4±0.4	$CH_2{=}C{=}CH_2$	12.5
	12.3±0.15	$CH_3C{\equiv}CH$	11.8
		1,3-C_4H_6	11.9
		$CH_3C{\equiv}CCH_3$	11.4
		cyclo-C_6H_{12}	13.0
$C_3H_4^+$	10.6±0.3	$CH_2{=}C{=}CH_2$	10.19
		$CH_3C{\equiv}CH$	10.3
		i-C_4H_8	11.62
$C_3H_5^+$	12.2±0.2	C_3H_6	11.9[c]
	12.0±0.15	*cyclo*-C_3H_6	12.1
		1-C_4H_8	11.70[c]
		cis-2-C_4H_8	11.6[c]
		trans-2-C_4H_8	11.76
		n-C_4H_{10}	13.15
		n-C_6H_{14}	12.5
$C_3H_6^+$	10.3±0.3	C_3H_6	9.7
		cyclo-C_3H_6	10.23
		n-C_4H_{10}	10.9
		i-C_4H_{10}	10.52
		n-C_5H_{12}	10.7
		i-C_5H_{12}	10.24
		n-C_6H_{14}	10.5
		$(CH_3)_2CH(CH_2)_2CH_3$	11.2
		$(CH_3)_2CHCH(CH_3)_2$	11.0
$C_3H_7^+$	10.5±0.3	*n*-C_4H_{10}	10.9[c]
		i-C_4H_{10}	11.0[c]
		n-C_5H_{12}	10.87
		i-C_5H_{12}	10.84
		n-C_6H_{14}	10.6[c]
		n-C_7H_{16}	11.36
		n-C_8H_{18}	11.09
$C_3H_8^+$	11.8±0.2	C_3H_8	11.2[c]
$C_4H_5^+$	12.8±0.2	*cyclo*-C_5H_8	13.4
		$CH_3C{\equiv}CCH_3$	12.2
$C_4H_6^+$	10.3±0.3	1,3-C_4H_6	9.24
		$C_2H_5C{\equiv}CH$	10.34
		$CH_3C{\equiv}CCH_3$	9.85
		cyclo-C_6H_{10}	11.2
$C_4H_7^+$	11.2±0.4	1—C_4H_8	11.07
		cis-2-C_4H_8	11.1
		trans-2-C_4H_8	11.24
		i-C_4H_8	11.32
		cyclo-C_5H_{10}	12.1
$C_4H_8^+$	9.8±0.3	1-C_4H_8	9.7[c]
		cis-2-C_4H_8	9.3[c]
		trans-2-C_4H_8	9.24
		neo-C_5H_{12}	10.32
		n-C_6H_{14}	10.3
		$(CH_3)_2CH(CH_2)_2CH_3$	10.5
		$(C_2H_5)_2CHCH_3$	10.5
		n-C_7H_{16}	10.9
		$(CH_3)_3CCH(CH_3)_2$	10.5
$C_4H_9^+$	10.8±0.35		
$C_5H_5^+$	13.6±0.2		
$C_5H_6^+$	9.76±0.15		
$C_5H_7^+$	10.80±0.12		
$C_5H_8^+$	9.8±0.3		
$C_5H_9^+$	11.2±0.2		
$C_6H_5^+$	14.6±0.35		

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[a] In electron volts.

[b] Literature appearance potentials have been taken from Ref. 42 except where noted.

[c] Average of values given by Field and Franklin (Ref. 42).

[d] W. A. Chupka and M. G. Inghram, J. Phys. Chem. **59** 100 (1955).

Table IV. Neutrals identified on the basis of mass spectra, appearance potentials, and/or percentage shutter effects.

CH_3	Methyl radical
CH_4	Methane
C_2H_2	Acetylene
C_2H_4	Ethylene
C_2H_5	Ethyl radical
C_2H_6	Ethane
C_3H_4	Allene and/or propyne
C_3H_6	Cyclopropane and/or propene
C_3H_8	Propane
C_4H_6	1-Butyne and/or 2-butyne
C_4H_8	1-Butene and/or other butenes
C_4H_{10}	Butane
C_5H_6	
C_5H_8	
C_6H_6	Benzene
C_6H_8	
C_6H_{10}	
C_6H_{12}	

saturated hydrocarbons such as methane, ethane, and propane. There is particular uncertainty in this conclusion because of the small shutter effects[38] and the consequent possibility that the appearance potentials are more representative of the background than the molecular-beam species.

In summary, reaction products for which there is evidence based on mass spectra, appearance potentials and/or percentage shutter effects are given in Table IV. Neutrals inferred from comparison of observed mass spectra with spectra taken at low temperatures are given in Table V.

Partial Pressures

Almost all of these compounds, particularly the high-molecular-weight ones, have been predicted[1–3] to be present only in quantities undetectable by the present method. Moreover, only highly unsaturated compounds rather than the type found, should have been observed.

To compare the observed with the predicted partial pressures $P(\mathrm{X})$ for various species X, observed ion currents were reduced to partial pressures using[32]

$$P(\mathrm{X})=[I^{+}(\mathrm{X})\,T]/[\gamma(\mathrm{X}_i)\,\sigma(\mathrm{X})\,S],$$

where $I^{+}(\mathrm{X})$ is the sum of all ion intensities due to X, T is the temperature of the reactor, $\gamma(\mathrm{X}_i)$ is the secondary electron multiplier gain for X^{+}, $\sigma(\mathrm{X})$ is the cross section for ionization of X, and S is the instrument sensitivity. A discussion of the possible error in these quantities is given in Ref. 35; probable error for the observed pressures given in Table VI are determined using tabulated equilibrium constants[44] and the observed hydrogen pressure. Since the spectrometer sensitivity is used to calculate both the observed hydrogen pressure and the observed hydrocarbon pressures, errors tend to cancel and probable error in the ratio between the two is less than a factor of 10.

Of the species given in Table VI, only C_2H, C_2H_2, and C_3 seem to be present in near-equilibrium concentrations; on the average, in all spectra measured, acetylene pressures were twofold less than predicted. For all spectra, partial pressures for CH_3, CH_4, and C_2H_4, however, are several orders of magnitude larger than predicted. Equilibrium constants for heavier molecules at these temperatures are not readily available. A rough approximation based on average bond energies and estimated entropy changes for addition of C or H_2 to an arbitrarily chosen molecule indicates that the partial pressure at this temperature and hydrogen pressure (10^{-4} atm) should decrease by three or more powers of 10 for each additional carbon or $-H_2$. The partial pressures of molecules heavier than those listed in Table VI, therefore, must also exceed the equilibrium pressures.

Formation of the Gaseous Molecules

That the observed ions do not result from either ion–molecule or molecular-beam reactions is shown by: (1) Partial pressures in the ion source were 10^{-6}–10^{-4} torr of hydrogen and generally less than 10^{-6} torr for hydrocarbons; ion–molecule reactions, however, are normally studied at pressures greater than 10^{-3} torr; (2) molecular flow conditions were expected for all but the highest pressures studied, precluding molecular-beam reactions; (3) a half-power hydrogen dependence was observed for most of the ions whereas both of the reactions in question require at least a first-power dependence; and (4) no shutterable high-molecular-weight ions were observed when the hydrogen–methane mixture was passed through the cold reactor at the highest

Table V. Neutrals identified only by comparison and subtraction of mass spectra.

CH_2	Methylene radical
C_2H	Radical
C_2H_3	Radical
C_4H_2	Diacetylene
C_4H_4	Vinylacetylene
$C_{10}H_8$	Naphthalene

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[44] *JANAF Thermochemical Tables*, D. R. Stull, Ed. (Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 1968), Document No. PB-168, 370.

pressures used in the experiments; (5) ion-source geometry is such that the opening at the point of ionization is large compared to the focus slits so that any ions formed from the reaction of free radicals with other species on the hot ion source escape and do not return as part of the molecular beam. That other sources of hydrocarbons or ions are not responsible for the results is indicated by: (1) Before hydrogen is introduced into the reactor, shutterable hydrocarbon ion intensities are not observed; this indicates that observed hydrocarbons are not degassed from the crucible; (2) when the ionizing electron beam is turned off, shutterable hydrocarbon ion intensity is not observed; this indicates that the "photo ion"[32] effect is not responsible for the ions; and (3) with changes in electron bombardment voltage (at constant temperature), the ion intensity signal is constant; this indicates that the ions are not formed by the electron bombardment heating.

Formation of radicals and other reactive intermediates in greater-than-equilibrium, steady-state concentrations is the best explanation of the large quantities of various species presently observed. Large steady-state concentrations of intermediates have been observed in the decomposition of compounds, and Gulbransen[11] has used this explanation for greater than equilibrium concentrations of hydrocarbons in a hot-graphite–cold-hydrogen experiment.

TABLE VI. Observed and predicted equilibrium pressures[a] of some of the species found in the high-temperature carbon–hydrogen reaction.[b]

Ion species	Ion intensity[c] (A)	Observed[d] pressure	Predicted pressure
H[e]	4.7×10^{-10}		
H_2	1.6×10^{-8}		
CH_3	1.3×10^{-11} [f]	3×10^{-8}	6×10^{-11}
CH_4	1.1×10^{-11}	2×10^{-7}	9×10^{-13}
C_2H	5.5×10^{-11}	1×10^{-6}	1×10^{-6}
C_2H_2	2.1×10^{-10}	4×10^{-6}	6×10^{-7}
C_2H_4	2.9×10^{-11}	4×10^{-7}	4×10^{-14}
C_3	7.4×10^{-12}	1×10^{-7}	6×10^{-8}

[a] In atmospheres; equilibrium constants from *JANAF*, Ref. 44.

[b] From Run 670405-2; see Fig. 4(b).

[c] Only the intensity for the parent peaks are given. These are uncorrected for secondary multiplier gains and ionization cross sections. Multiplier gains for *m/e* 12 and above are about 10^5.

[d] Calculated from the relationship $P=(I^+T)/(\sigma\gamma S)$; see text.

[e] The H/H_2 ratio was used to calculate spectrometer sensitivity.

[f] This is 1/20 the observed intensity at *m/e* 15. The C_2H_2 and C_2H_4 calculated pressures are not corrected for fragmentation from heavier species.

Because of the extreme complexity of the product mixture presently found, a detailed mechanism for the formation of the hydrocarbons from the elemental species H, H_2, C, C_2, and/or C_3 is not readily deduced. The role of C_2^- [39,44] and negative ion products, which could not be observed, is not known. Observed products, however, suggest a number of mechanism steps.

The reactions of atomic carbon and C_3 with hydrogen, and with various gaseous and condensed hydrocarbons have been found[16–31] to include a number of addition or insertion steps. Such reactions have been postulated for hot-carbon–cold-hydrogen reactions under exploding wire[14,15] and microwave-discharge[45] conditions and are likely to have occurred under the present conditions.

Possible reaction steps are suggested by work of MacKay, Wolfgang, and co-workers,[16,17] in which atomic carbon is reacted with gaseous methane, hydrogen, and ethylene. They found that atomic C reacts with methane to form both ethylene and acetylene. With both hydrogen and ethylene present, they found that atomic C inserts into H_2 to form CH_2, CH_2 inserts into or adds to C_2H_4 to form propene or cyclopropane (C_3H_6, mw=42), CH adds to and/or inserts into C_2H_4 to form C_3H_5 (mw=41), CH_3 adds to C_2H_4 to form C_3H_7 (mw=43), and C adds to and/or inserts in C_2H_4 to form propyne or allene (C_3H_4, mw=40). In the present spectra, the addition of methane to the reactant gas results in increased intensity of the CH_x^+ ions; this probably corresponds to the formation of CH_x (except perhaps CH) radicals. Increased intensities of the $C_2H_x^+$ ions relative to $C_2H_2^+$ could be due to reactions of CH_x ($x=0$–4) species with one another, i.e., $C+CH_4\rightarrow C_2H_4$. The $C_3H_x^+$ ions observed could result from reactions cited by MacKay *et al.*[17], since relative intensities of molecular ions corresponding to the C_3H_x compounds all increase when methane is added. Of these ions, $C_3H_4^+$, which would be formed by the reaction of atomic C with C_2H_4, shows the smallest increase. These reactions, however, need not be the only mode of formation of the above compounds in the present system; because of the large concentrations of the reactants, the reaction $CH_3+C_2H_2\rightarrow C_3H_5$ also may be responsible for the increase of $C_3H_5^+$ relative to $C_3H_3^+$. These mechanism steps are in agreement with the observation that increased hydrogen pressure results in the decreased importance of high-molecular-weight hydrocarbon ions (Fig. 4); at the higher pressures, reaction of a hydrocarbon with hydrogen gas becomes more probable.

Additional support for these mechanism steps is found in the observation of greater-than-equilibrium concentrations of BH_3 and BH_2R (R is CH_3 and/or C_2H_5) formed in the reaction of H_2 with boron carbide at 2000°.[35] This is explained by the insertion of BH,

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[45] M. M. Shahin, Nature 195, 992 (1962).

which is isoelectronic with C, into H_2, CH_4, and C_2H_6, respectively.

Correlation of the observed results with decomposition steps is difficult. The observation of large concentrations of high-molecular-weight compounds, however, does indicate that the decomposition process is slow relative to the formation of the hydrocarbons and to the 80-msec contact time. That hydrocarbons once formed are not easily decomposed at high temperatures is suggested by observations made during the formation of pyrolytic graphite from hydrocarbons.[40]

Decomposition behavior in the present carbon–hydrogen work appears related to the condensation barrier observed in plasma chemistry experiments[46] and to the nucleation reaction[47,48] observed in the pyrolysis of small hydrocarbons at about 1000°–1500°. The condensation barrier, as described by Reed,[46] results because formation of a less stable gas-phase species occurs more rapidly than the formation of the thermodynamically favored condensed-phase species which require nucleation. In the pyrolysis of small hydrocarbons, a number of high-molecular-weight hydrocarbons, as well as soot, are often obtained.[47,48] Flame studies[49] of the formation of soot from various hydrocarbons also show a buildup of hydrocarbons; soot formation, however, is shown to depend on the presence of radicals as well as high-molecular-weight polyacetylenes.

DISCUSSION

In comparing the present work with other work done on the high-temperature carbon–hydrogen reaction, several differences should be noted. Hydrogen pressures used in the present experiments are much lower than most used in previous studies, and the formation of high-molecular-weight hydrocarbons becomes relatively less important with increasing hydrogen pressure (Fig. 4). Because the geometry of the reactor and sample, as well as contact times, will result in different numbers of collisions, products may differ from one study to another. Possible catalysis[5] by trace metals in various graphite samples used could also lead to different results. Finally the method of sampling the reaction should result in some differences, particularly between those experiments in which the reaction is directly analyzed and those in which quenched products are analyzed.

In the previous work most comparable to the present study, Chupka *et al.*[8] examined the high-temperature (2000°K) carbon–hydrogen system using an integral furnace mass spectrometer to determine the heat of formation of the methylene radical. Reactants included both the elements and a series of hydrocarbons at pressures up to 1 torr. Although they found evidence for small quantities of a number of radicals including CH, CH_2, CH_3, and C_2H, no comment is made about high-molecular-weight ions such as those observed in the present experiment. When hydrocarbons were pyrolyzed, concentrations of the radicals were larger than predicted for gas–solid equilibrium; reproducible equilibrium constants in agreement with presently[50] known thermodynamic data were obtained when only gas-phase species were considered. The heat of formation for methylene determined from the gas-phase reaction $CH+CH_3 \leftrightarrows 2CH_2$ is within experimental error of the presently accepted[50] value, 91.8 kcal/mole; however, the value determined from $C(s)+H_2 \leftrightarrows CH_2$ is 13.5 kcal/mole too exothermic, i.e., CH_2 is present in 10–30-fold excess over equilibrium concentrations. Lifshitz and Chupka[50] suggest that this discrepancy might arise from use of incorrect ionization cross sections and pressures. This excess concentration is, however, in direct agreement with the present results.

Other hot-graphite–hot-gas studies include carbon tube experiments by Plooster and Reed[6] and by Ievleva,[9] and carbon arc experiments by Baddour and Iwasyk[7] and by Baddour and Blanchet.[2] Temperatures ranged between 1800° and 4500°K while hydrogen or hydrocarbon pressures ranged between 0.25–45 atm. In all of these experiments, the reacting mixture was sampled through hypodermic needle probes and quenched; soot or carbon deposits on these probes were reported in all but Ievleva's high-pressure experiments. Unsaturated products were obtained in all but the high-pressure work; products, other than acetylene, included diacetylene,[6,7] vinylacetylene,[7] and benzene.[7] In one set of experiments,[7] ethylene as well as acetylene was found in high concentrations. These experiments, which in general show acetylene to be the major product, do not appear to be in disagreement with the conclusions based on the present work because of the different conditions, particularly the much higher hydrogen pressure, and the analysis of quenched products rather than direct analysis of the reaction mixture. The formation of products other than acetylene, particularly of soot correlates with the formation of high-molecular-weight molecules observed in the present work.

Hot-graphite–cold-gas studies include reactions of heated graphite rods,[4] filaments,[12] or chunks,[10,11] or of exploding graphite filaments[14,15] with hydrogen or hydrocarbon atmospheres; a microwave discharge experiment[45] also appears to be of this type. Pressures

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[46] T. B. Reed, in *Advances in High Temperature Chemistry*, L. Eyring, Ed. (Academic Press Inc., New York, 1967), Vol. 1, pp. 260–316.

[47] H. B. Palmer, J. Lahaye, and K. C. Hou, J. Phys. Chem. **72**, 348 (1968).

[48] C. F. Cullis and N. H. Franklin, Proc. Roy. Soc. (London) **A280**, 139 (1964).

[49] U. Bonne, K. H. Homann, and H. G. Wagner, Symp. Combust. 10th, Univ. Cambridge, Cambridge, Engl., 1964, 503 (1965).

[50] C. Lifshitz and W. A. Chupka, J. Chem. Phys. **48**, 1109 (1968).

were normally near atmospheric and temperatures ranged from about 1200°C to the extremely high ones of an exploding wire. Soot or "carbon" formation is mentioned in several studies[10,11,13,45]; the reported products include methane,[4,11,12,15] acetylene,[4,11,12,15] ethylene,[4,11,12] ethane,[12,15] propane,[12] butanes,[15] benzene,[11,15] and toluene.[11] Involatile and/or solid products, if present, might not have been detected. Gulbransen[11] discussed the formation of this wide variety of products in terms of a flow reaction; other authors[14,15,45] discussed the formation of the product molecules in terms of addition–insertion reaction mechanism steps. Clarke and Fox,[12] however, have discussed their results in terms of a surface reaction. In general, this approach to the study of the high-temperature carbon–hydrogen system gives results that are similar to those observed in the present study.

Evidence for the addition–insertion mechanism for high-temperature-generated carbon species and for nuclear-generated carbon atoms has been reported previously.[16–31] The present study, however, seems to be the first to suggest the importance of these mechanism steps in the high-temperature reaction of carbon and hydrogen.

The extreme importance of the nucleation reaction or condensation barrier in the high-temperature carbon–hydrogen reaction is indicated by the large number of high-molecular-weight hydrocarbon ions observed in this study. This buildup of hydrocarbons appears to have implications for diverse areas including the formation of soot and other species as air pollutants, and the formation of hydrocarbon species under paleochemical conditions. Gulbransen[11] has briefly discussed the latter. Further experiments are underway to determine the products of the high-temperature carbon–hydrogen–nitrogen flow reaction since both nitrogen and ammonia, as well as hydrogen and methane, are thought to have been present in the primeval atmosphere.

Although the present study is not the first Knudsen cell experiment in which difficulties in achieving equilibrium concentrations of vapors were recognized, the small orifice used in these experiments reinforces the necessity of extreme caution in the interpretation of such experiments.

SUMMARY

Direct mass-spectrometric analysis of the effluent from a flow reactor at 1880°–2430°K containing graphite and hydrogen has indicated the presence of a large number of hydrocarbons with molecular weights to 140 and above. The most abundant molecules appear to include unsaturated, acyclic, nonaromatic compounds; evidence for some radicals is obtained. Low-molecular-weight hydrocarbons that are identified have, in general, been found in other high-temperature experiments. The high-molecular-weight species found are thought to arise as part of a steady state in the crucible reactor. Reasonable mechanism steps for the formation of the hydrocarbons include insertions and additions of C, C_3, and hydrocarbon radicals to hydrocarbon molecules present in the reactor.

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