# PYROLYSIS OF SIMPLE HYDROCARBONS IN SHOCK WAVES<sup>1</sup>

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Shock waves have been used to produce rapid, homogeneous heating in simple hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>,

## Introduction

Porter<sup>2</sup> has suggested that the formation of solid carbon and hydrogen which occurs in the pyrolysis of hydrocarbons at temperatures above about 1000° proceeds by a series of degradations to acetylene. This acetylene then simultaneously polymerizes and loses hydrogen to form carbon. A large amount of work has been devoted to the study of high temperature reactions of hydrocarbons<sup>3</sup> but there is as yet no agreement on any particular mechanism. For instance, in contrast to Porter's ideas Parker and Wolfhard<sup>4</sup> have suggested that large hydrocarbon polymers, built up by polymerization reactions, ultimately condense to liquid droplets. These droplets then lose hydrogen and take on a graphitic structure.

Many of the experiments which have been performed are hard to interpret because surface reactions may enter to an uncertain extent and the heating and cooling times are either relatively long or not well known.

In this paper we describe experiments on hydrocarbon pyrolysis in which the heating was produced by a shock wave generated in a shock tube. The heating is homogeneous, the heating time is extremely short (approx.  $10^{-8}$  sec.) and the cooling time fairly short (approx.  $10^{-4}$  sec.). This means that products isolated after the shock may be more representative of intermediates in the pyrolysis reaction than is the case for other ways of heating. The results are consistent with Porter's mechanism and provide evidence that diacetylene may be the first major intermediate formed from acetylene.

**Conditions for Experiments.**—For the first set of experiments (see Table III) it was decided to compare several hydrocarbons under conditions of temperature and concentration as nearly equivalent as possible. In a shock tube most of the pyrolysis reaction occurs in the high temperature  $(T_5)$  and pressure  $(P_5)$  region behind the reflected shock wave (see diagram in Fig. 1) and it seemed reasonable to compare the different hydrocarbons

(3) See review by A. G. Gaydon and H. G. Wolfhard, "Flames," Chapman and Hall, London, 1953; E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, and F. Cabannes, J. Phys. Radium, **17**, 492 (1956).

(4) W. G. Parker and H. G. Wolfhard, J. Chem. Soc., 2038 (1950).

at equal values of  $T_5$  and equal partial pressures. For simplicity and because the kinetics and extent of reaction were unknown, the calculations of temperatures and pressures behind incident and reflected shocks for various shock strengths were based on the assumption of complete vibrational equilibration but no chemical reaction. This should be a reasonable picture of the early stages of the reaction but becomes less realistic as the pyrolysis proceeds.

The results of the present work suggest a first reaction like  $2C_2H_2 \rightarrow C_4H_2 + H_2$ . Although the heat of this reaction apparently has not been measured, it has been estimated<sup>5</sup> to be nearly thermally neutral. Also there is no resulting change in total pressure. For these reasons and the relatively small amount of reaction observed the assumption of no reaction in the calculation of the hydrodynamic properties should be less serious than would usually be expected.

The calculations were made for two final temperatures  $T_5 = 1900$  and  $2500^{\circ}$  K. for an initial temperature  $(T_1)$  of  $300^{\circ}$  K. To achieve these temperatures with even the relatively simple hydrocarbons used in this study it is necessary to reduce the average heat capacity of the gas. This was done here by making mixtures with argon. The concentration for each hydrocarbon was selected by requiring that the enthalpy of the argonhydrocarbon mixture be equal to that for 20%  $C_2H_6$ -80% A at 2200° K. This should make the hydrodynamic properties of the mixtures reasonably comparable and tend to provide similar rates of cooling.

Then the shock wave conservation equations for mass, momentum and energy were solved with the ideal gas equation of state and the National Bureau of Standards values of  $H^0-H^0_0$  for the hydrocarbons.<sup>6</sup>

The tabulated values were extended to  $2500^{\circ}$  K. using the harmonic oscillator approximation and the vibrational assignments quoted in references in the NBS tables.

The equations were conveniently solved for the incident shock by the method of Bethe and Teller<sup>7</sup> and then the appropriate reflected shock was found by requiring that  $(u_1 - u_2)$  of the incident

(5) E. A. Westbrook, K. Hellwig and R. C. Anderson, "5th Symposium (International) on Combustion," Reinhold Publ. Corp., New York, N. Y., 1955.

(7) H. A. Bethe and E. Teller, "Deviations from Thermal Equilibrium in Shock Waves," reprinted by the Engineering Research Institute, University of Michigan.

<sup>(1)</sup> This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. 49(638)-167 and by the Office of Naval Research. Reproduction in whole or in part is Dermitted for any purpose of the United States Government.

part is permitted for any purpose of the United States Government. (2) G. Porter AGARD Memo. AG 13/M9(1954), "The Mechanism of Carbon Formation," also 4th Symposium (International) on Combustion. Williams and Wilkins, Baltimore, Md., 1952, p. 248.

<sup>(6)</sup> Selected Values of Properties of Hydrocarbons, Circular 461, National Bureau of Standards, Washington 1947.

shock be equal to  $-(u_1 - u_2)$  of the reflected shock where u is the flow velocity relative to the shock front. This condition is equivalent to requiring zero flow velocity behind the reflected shock. Because of the assumption of no reaction there was no change in the number of moles of any reactant and the results are independent of pressure. Thus only a shock velocity need be specified to fix a  $T_5$ . Finally the starting pressure,  $P_1$ , was chosen for each mixture so as to give the same concentration (moles/l.) of hydrocarbon in the hot region behind the reflected shock.

Table I shows the results of the calculation. Subscripts 1, 2 and 5 refer to the gas ahead of the incident shock, behind the incident but ahead of the reflected shock, and behind the reflected shock respectively.  $u_1$  is the velocity of the incident shock and  $\rho$  is the density.  $P_4/P_1$  is the pressure ratio across the diaphragm in the shock tube for hydrogen in the high pressure section. This ratio was determined by matching the flow velocity  $(u_1 - u_2)$  and pressure in the hot hydrocarbon to the same quantities produced by an expansion wave in the hydrogen. The hydrogen was taken to have its equilibrium heat capacity  $(C_v = C_v(T))$  which introduces only a small correction to the usual assumption of  $\gamma = 1.4.8$ 

#### TABLE I

# SHOCKS IN HYDROCARBON-ARGON MIXTURES

Calculations based on ideal gas, vibrational relaxation but no reaction:  $T_1 = 300$ °K. Incident and Reflected Shocks. Composition chosen to give mixtures same enthalpy at 2200°K.

	$T_{2}$ .		141.			$P_4/P_1$
Composition mole fr. HC	$\stackrel{\circ K}{\pm 5}$	7₅, °K.	$mm./\mu sec.$ $\pm 0.003$	$p_1/\rho_1 \pm 0.05$	$ ho_{s}/ ho_{1} \pm 0.2$	$H_2 \stackrel{\text{driver}}{\pm 3}$
$0.366 C_2 H_2$	1093	1900	1.278	5.44	20.7	65
$.366 C_2 H_2$	1396	2500	1.521	6.06	25.0	127
$.288 \mathrm{CH}_{4}$	1092	1900	1.306	5.32	20.1	66
$.288 \text{ CH}_{4}$	1403	2500	1.546	6.14	25.1	132
$.265 \mathrm{C_2H_4}$	1128	1900	1.285	5.64	22.8	70
$.265 C_{2}H_{4}$	1438	2500	1.543	6.44	28.6	145
$.200 \ C_2 H_6$	1140	1900	1.286	5.71	23.8	74
$.200 C_2 H_6$	1442	2500	1.555	6.67	30.9	156
.166 C <sub>6</sub> H <sub>6</sub>	1144	1900	1.300	7.38	38.2	104
$.166 C_{6}H_{6}$	1457	2500	1.562	8.45	48.1	213

#### TABLE II

## SHOCKS IN ACETYLENE

Calculations based on ideal gas, vibrational relaxation but no reaction.  $T_1 = 300^{\circ}$ K. Incident and reflected shocks.

<i>T</i> ₂, °K. ±5	<i>T</i> ₅, °K.	$\begin{array}{c} u_1,\\ \mathrm{mm./\mu sec.}\\ \pm 0.003 \end{array}$	$_{\pm 0.05}^{ ho_2/ ho_1}$	$_{\pm 0.2}^{ ho_5/ ho_1}$	$P_4/P_1$ (H <sub>2</sub> driver)
300	300	0.345			
557	800	1.022	5.31	22.4	25
663	1000	1.234	6.53	32.1	48
772	1200	1.425	7.51	41.0	82
879	1400	1.597	8.30	49.0	131
988	1600	1.762	9.01	56.5	206
1095	1800	1.914	9.63	63.5	300
1262	2100	2.132	10.41	73.2	603
1472	2500	2.395	11.32	84.6	1314

The second series of experiments (Table IV) was done only with pure acetylene but under a variety

(8) E. F. Greene and J. P. Toennies, "Chemische Reaktionen in Stosswellen," Steinkopf (in press).



Fig. 1.—Time-distance diagram of shock interaction with end plate and contact surface.

of conditions. Table II lists the corresponding calculated properties for this kind of shocks. The same assumptions were used as for Table I.

## Experimental

The experiments were carried out in a 3" i.d. shock tube similar to one described earlier.<sup>9</sup> The low pressure section was a 7-foot length of Pyrex pipe and the high pressure section was either a 50 or 100 cm. length of brass tubing. One to four pieces of Koda-trace sheeting were used for a diaphragm to separate the two sections. Before a run the tube could be evacuated to about 3  $\mu$  and had a leak rate of about 1  $\mu$ /min. When the two sections had been filled with the desired gases the shock was set off, within five minutes of the end of pumping, by bursting the diaphragm with a needle. Beginning immediately after the shock was fired, the contents of the tube were pumped out through two traps cooled in liquid nitrogen. This permitted the separation of the condensable gases from the hydrogen driver gas. The final pressure achieved was from a few microns up to several hundred microns because of varying leaks at the ruptured diaphragm. Pumping was stopped after about 2 hours.

For the first series of experiments (Table III) the hydrocarbons were CH<sub>4</sub>,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$  and  $C_6H_6$ . The manufacturer listed purities as 0.99, 0.995, 0.95, 0.95 and reagent grade, respectively. The gases were used without further purification except that the acetylene was bubbled through concentrated sulfuric acid to remove the solvent acetone. The gases (taken as ideal) were mixed with varying amounts of argon using a mechanical stirrer in a bulb. After the products were condensed in the traps, the procedure was to warm the condensate to room temperature and measure the pressure in a known volume. Two aliquots were then used for analysis in a gas chromatograph with silica gel and di-*n*decyl phthalate columns, respectively. The first column resolved the  $C_2$  hydrocarbons and the second separated  $C_2$ from  $C_3$  and resolved the  $C_4$  hydrocarbons. The sensitivity of the thermal conductivity detector was calibrated with known mixtures of the gases. In this way it was possible to determine relative amounts of individual  $C_2$  and  $C_4$  and total  $C_3$  hydrocarbons in the products. The total amounts

(9) E. F. Greene, J. Am. Chem. Soc., 76, 2127 (1954).

## TABLE III

PRODUCTS RECOVERED FROM SHOCKS IN HYDROCARBON-ARGON MIXTURES

Mole % of original hydrocarbon recovered as each product (assuming no reaction in 10% of tube

				Mole %	oi origina	l hydroca	rbon recov	ered as	each pro	oduct (a	ssuming i	10 reaction	1 IN 10%	, or tube
Original								behind	d end pl	ate)			Total	
mole fraction HC $\pm 0.002$	$P_1$ $\pm 0.2$ , mm.	$P_4/P_1\pm 2$	$u_1, \text{ mm./} \\ \mu \text{sec.} \\ \pm 0.01$	C2H6	$C_2H_4$	$C_2H_2$	All C:	C4H2	C4H4	C₄Hs	C4H3	C4H10	C <sub>2</sub> thru C <sub>4</sub>	Car- bon
$0.368 C_2 H_2$	22.4	86				77	<0.01	2.9	0.8	0	0	<0.18	81	Small
$.366 C_{2}H_{2}$	23.7	85	>1.03	0	0	95	0	1.4	1.8	0	0.04	.09	97	Small
$.368 C_2 H_2$	18	164				50	0.07	3.2	0.3	0	0	.03	<b>54</b>	Med.
$.366 C_2 H_2$	19.2	162		0	0	59	.10	5.1	.44	0.18	0.44	.09	65	Large
.289 CH <sub>4</sub>	30.5	88	1.234	3	0.12	0.12	.3		.07	.08	.05	.4	4.1	
.289 CH <sub>4</sub>	21.1	174	1.54	0.96	4.3	15	.3	1.3	.5	.2	.02	<b>2</b>	23	$\mathbf{Small}$
$.265 C_{2}H_{4}$	28.9	98	1.233	.1	84	4	0	0	.2	.9	0	0.3	90	
$.265 C_2H_4$	21.3	182		.04	60	22	0.15	0.6	.12	.8	0	.5	86	None
.199 C <sub>2</sub> H <sub>6</sub>	36.0	108	1.22	56	36	.4	1	0	.09	.6	.15	. 15	95	None
.199 C <sub>2</sub> H <sub>6</sub>	28.4	209	1.444	33	36	10.4	1.4	0.3	1.2	1.2	.05	1.1	83	
.196 C <sub>2</sub> H <sub>6</sub> +	27.8	203	1.445	26	43	16	1.6	.27	1.2	1.2	.08	1.8	91	None
0.0046 NO														
.166 C <sub>6</sub> H <sub>6</sub>	28.5	138		0.5	<b>4.4</b>	8.8	0.4	.22	0.1	0.14	0	0.8	15	$\mathbf{Small}$
.166 C <sub>6</sub> H <sub>8</sub>	21.7	272	≤1.475	0.4	<b>2</b>	19	0.14	1.0	0.3	.14	0.007	0.3	23	Med.

TABLE IV

PRODUCTS RECOVERED FROM SHOCKS IN ACETYLENE

						T	Fraction of available C <sub>2</sub> H <sub>2</sub> recovered as				
<i>P</i> 1, mm.	P4/P1 (H2 driver)	$u_1, \text{ mm./} \\ \mu \text{sec.} \\ \pm 0.1$	$T_{5}, ^{\circ}K. \pm 120$	ρε/ρι ±3	$t_{ m m},\ \mu{ m sec.}\ \pm 5$	pressure section, cm.	$C_2H_2$	$C_4H_2$	conden- sables	Total recovery	
4.6	1250	2.31	2365	80.8	73.5	50	0.55	0.055	0.29	0.90	
4.7	615	2.03	1957	68.6	91.6	50	.84	.018	. 18	1.04	
4.7	319	1.78	1627	57.2	115.6	50		.007	. 10	• • •	
8.26	367	1,83	1694	59.6	110.2	50	.74			••	
2.16	677	2.06	2000	70.0	89.0	50	.79	.037	.64	1.45	
4.13	709	2.08	2026	70.8	87.6	100	.68	.54	.30	1.03	
3.91	745	2.10	2053	71.7	86.2	25	.60	••			
4.04	727	2.09	2040	71.2	87.0	50	.62	.059	.08	0.75	
2.56	573	2.00	1915	67.2	94.0	50	.81	.072	.11	. 99	
7.97	745	2.10	2053	71.7	86.2	50	.56	.030	.23	.82	
3.95	380	1.84	1706	60.0	109.0	50	.91	.027	.12	1.06	
3.94	1500	2.38	2477	83.8	69.5	50	.66	.077	.41	1.15	
3.94	745	2.10	2053	71.7	86.2	25	.66	.054	.25	0.96	
3.96	740	2.10	2053	71.7	86.2	100	. 59	.027	.22	0.83	

of each were found by assuming that the total pressure was the sum of the partial pressures of  $C_2$  through  $C_4$ . The fraction of each starting hydrocarbon recovered in the trapping procedure when no shock was set off was found to be 0, 0.92, 1.0 and 1.0 for  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$ , respectively. Therefore no methane appeared in the products and the measured amount of ethane recovered was multiplied by 1/0.92. In general there was no change in the relative concentrations of the components as determined by the gas chromatograph after the sample had stood overnight at room temperature, with the exception of a slight decrease for C<sub>4</sub>H<sub>2</sub>.

For the experiments listed in Table IV the only gas used was pure acetylene, and the procedure for setting off the shocks was as described above. After the products had been condensed in the liquid nitrogen traps, they were warmed to Dry Ice and room temperature and the pressure measured each time in a known volume. At Dry Ice tem-peratures acetylene was the only volatile substance so its pressure was obtained directly. The difference in the Dry Ice and room temperature pressures indicated very roughly the amount of diacetylene and other similar substances such as vinylacetylene. The mixture was then condensed at liquid nitrogen temperature into a small cold finger. The finger temperature was then raised to that of a Dry Ice-bath which let the acetylene pass to another part of the system. The cold finger was sealed by turning a stopcock and re-moved (ground glass joint) from the system for weighing. This gave the weight of condensables other than acetylenc. The contents of the cold finger were extremely unstable and traces left in the finger became discolored after standing a few hours at room temperature. After the weighing the

finger was reattached to the system and the contents and the C<sub>2</sub>H<sub>2</sub> were condensed into an infrared cell. After the cell was warmed and the gases were mixed by moving a small amount of mercury in and out of the finger, the infra-red spectrum was recorded in the NaCl region. In the shock products only bands of  $C_2H_2$  and  $C_4H_2$  were observed, although occasionally a small amount of water appeared due to leaks from the atmosphere during the pumping or from water vapor in the hydrogen cylinder. A correction for the water was made where necessary. The calibrated intensivaried from 0.2 to 1.0 of the amounts which would have provided the measured pressure differences for the room temperature and Dry Ice points. Thus there may be other C4 or higher hydrocarbons present although the precision is not high.

The hotter acetylene shocks produced bright yellow flashes of light (with a continuous visible spectrum) and large quantities of carbon. Both the amount of light and carbon decreased at lower temperatures and in progressing from  $C_2H_2$ , to  $C_8H_6$ ,  $CH_4$ ,  $C_2H_4$  and  $C_2H_6$ .

A schlieren system for detecting the passage of weak shocks in the hydrocarbons was being developed during the course of these experiments and for this reason some velocities are not available for the experiments in Table III. For the experiments of Table IV the velocities were not measured but were estimated from the measured  $P_4/P_1$ , with the help of a graph of  $P_4/P_1$  vs.  $u_1$  obtained from other similar shocks in acetylene in the same apparatus. This is perhaps satisfactory here but probably contributes significantly to the scatter of the results.

#### Results

The results of the two series of experiments are presented in Tables III and IV. It is clear from the available velocities in Table III that in general the actual shocks were somewhat weaker than the ones for which the calculations were made. A rough estimate would be that the actual  $T_5$ 's were about 1800 and 2400° K. Nevertheless the calculations may be used with rough corrections in view of the noticeable scatter in the product analyses. This scatter is probably due to several factors which are: (1) non-uniform bursting of the diaphragm. Variation of  $u_1$  for a given  $P_4/P_1$  may amount to  $\pm 0.1$  mm./ $\mu$  sec. or  $\pm 120^{\circ}$  K. in  $T_6$ . (2) Losses in the recovery process. Particularly in the case of benzene shocks the pumping out was slow and a considerable amount of high boiling material may have been left behind. (3) The difficulty in analyzing the samples which are of the order of millimoles. The first is likely to be the most serious source of error and could be reduced with more successful velocity measurements.

The size of the fluctuations which can arise may be seen from the first two series in which under nearly identical starting conditions the fraction of acetylene recovered was 0.77 and 0.95.

Dashes in the table indicate that the particular measurement was not made successfully for that run. On five of the runs for which velocity measurements were attempted (Table III) one photomultiplier tube observed the emitted light at the end plate. The width of the peak at half height varied from 140 to 250 sec. and the average was 170 sec.

In one run a small amount of NÖ was added to an ethane-argon mixture. There was no significant difference in the products recovered.

The runs of Table IV were performed with  $C_2H_2$ because all the indications from Table III are that the other hydrocarbons first break down to  $C_2H_2$ . For instance, in the  $C_2H_6$  and  $CH_4$  shocks large fractions of  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$  were recovered, while for  $C_2H_4$  shocks there were only  $C_2H_4$  and  $C_2$ - $H_2$ , and for  $C_2H_2$  shocks only  $C_2H_2$  of the three  $C_2$ hydrocarbons.

A few experiments were used to test the dependence of the amount of decomposition on the length of the high pressure section. The normal 50 cm. section was replaced with a 100 cm. section which contained a movable plunger so that the effective length could be shortened to 25 cm. Figure 2 shows the result that at a constant  $P_4/P_1$  the amount of  $C_2H_2$  used up is roughly independent of the length of the high pressure section. This means that the heating time is not ended by the return of the rarefaction wave from the high pressure end even with a 25 cm. section.

An important parameter for any reaction is the length of time the mixture is exposed at the given temperature and pressure. Unfortunately this time is usually difficult to determine precisely in shock tube experiments;<sup>10</sup> nevertheless, an esti-



Fig. 2.—Dependence of amount of acetylene undergoing reaction on length of high pressure section.



Fig. 3.—Dependence of amount of acetylene undergoing reaction on pressure behind reflected shock. Numbers indicate calculated curves for first, second and third order reactions.

mate can be made in the present work because of a fortunate circumstance. In general the flow pattern near the end plate in a shock tube may be represented by the diagram in Fig. 1. The reflected shock first heats the gas nearest the end plate and then moves back toward the contact surface. At the contact surface a shock is transmitted into the cold driver gas ( $H_2$  in our case) and either a rarefaction or a shock is reflected back toward the end plate. When a shock is reflected, further heating occurs and the temperature history becomes particularly complex because deviations from one dimensional flow become considerable. On the other hand when a rarefaction wave is reflected. cooling begins and if the cooling is sufficient the reaction may be considered to be stopped. We have used the criterion for a rarefaction to be reflected that

## $\gamma_{\rm H_2} \rho_{\rm H_2} < \gamma_{\rm C_2H_2} \rho_{\rm C_2H_2}$

and

flected shock temperature because drum camera pictures usually show significant emission only for the first reflection. Further reaction in these lower temperature pulses should make no appreciable change in the composition of the products isolated from the reaction.

<sup>(10)</sup> An exception is the case of the "tailored-interface" method of H. S. Glick, J. J. Klein and W. Squire, J. Chem. Phys., 27, 850 (1957). Their "chemical shock tube" also avoids reheating the reaction mixture on subsequent reflections of the shock back and forth between the ends of the shock tube. In our experiments we believe these secondary pulses produce temperatures much lower than the original re-



Fig. 4.—Variation of rate constant for acetylene reaction with reciprocal temperature. Lines show slopes for activation energies of (1) 27 and (2) 37 kcal./mole.



Fig. 5.-Free energies of formation vs. temperature.

 $(\gamma + 1)_{H_2} \rho_{H_2} < (\gamma + 1)_{C_2H_2} \rho_{C_2H_2}$ 

where  $\gamma$  is the ratio of specific heats.<sup>11</sup> Here the

properties of the gases are to be compared on both sides of the contact surface—that is, the hydrogen has been cooled by expansion and the acetylene heated by the incident shock. This condition is easily satisfied for all the runs in both series except the two hottest ones in Table IV. Therefore we take as a reasonable approximation that the heating time is a linear function of the distance of the gas from the end plate.

$$t = t_{\rm m}(L - X) \qquad 0 \leq X \leq L$$

 $t_{\rm m}$  and L are defined in Fig. 1 and X is the distance along the shock tube from the end plate. Here the rarefaction is taken as moving immediately from the contact surface to the end plate and as suppressing further reaction entirely. Neither of these conditions is met but we feel that the actual heating times are to a reasonable extent proportional to the ones calculated on this basis.

It may be shown that for ideal shock tube behavior  $t_{\rm m}$  is given by

$$t_{\rm m} = \mathbf{X} \left(\frac{\rho_5}{\rho_2} - 1\right) / \left[ u_1 \left(\frac{\rho_5}{\rho_1} - \frac{\rho_5}{\rho_2}\right) \right]$$

where **X** is the length of the low pressure section. Again the behavior of the real shock tube will deviate (shorter  $t_m$  by a factor of about 2) from the estimate but various values of t should be in approximately the right ratios. In two runs in acetylene-argon mixtures in which a photo tube observed the emitted light at the end plate the light pulse was roughly triangular and the base measured 240 and 160  $\mu$ sec. The calculated values of  $t_m$  are 273 and 211  $\mu$ sec., respectively, which is certainly as good agreement as could be expected.

A number of drum camera streak schlieren pictures were made for shocks with  $u_1$  from 1.47 to 2.22 mm./ $\mu$ sec. These show the incident and reflected shocks clearly but unfortunately a detailed comparison with Fig. 1 is hard to make at later times because of the emitted light and absorption from the carbon. Nevertheless, the time for light emission and the flow pattern for the whole range of  $u_1$ seem to be consistent with the presence of a reflected rarefaction wave at the contact surface.

Several runs were made at approximately the same  $P_4/P_1$  but different starting pressures in order to show the pressure dependence of the  $C_2H_2$  reaction. The fractions of the available  $C_2H_2$  (the amount originally in the shock tube behind the end plate was assumed not to react) which disappeared in the reaction are plotted as open circles in Fig. 3 against the pressure behind the reflected shock. The filled circles indicate runs in which  $Ar-C_2H_2$  mixtures were used.

For comparison three curves are also included. These curves were calculated assuming that acetylene disappears only by reacting with itself in a first-, second- or third-order reaction and that there is no back reaction. All the curves were arbitrarily matched to the average of the points in the center of the graph. The fact that various parts of the acetylene sample are heated for various times means that for the second- and third-order cases the integrated rate law must be integrated

(11) W. G. Penney and H. H. M. Pike, Repts. Prog. Phys., 13, 46 (1950).

again from 0 to  $t_{\rm m}$ . For instance for the secondorder case where A is the concentration of acetylene  $dA/dt = -kA^2$ 

gives

$$[(A_0 - A)/A_0]t' = A_0 k t'/(A_0 k t' + 1)$$

for a particular t'. Then

$$\left(\frac{A_0 - A}{A_0}\right)_{\text{Total}} = \frac{1}{t_m} \int_0^{t_m} \frac{A_0 kt'}{A_0 kt' + 1} dt' = 1 - \frac{\log\left(1 + A_0 kt_m\right)}{A_0 kt_m}$$

This and the similar case for the third-order reaction are the curves plotted in Fig. 3.

The second-order curve seems to give the best fit to the experimental points although the scatter leaves some doubt about the choice.

Finally the calculated partial pressures of acetylene  $(P_{C_{2H.}})_5$ , the second-order rate law, and the calculated values of  $t_m$  were used for a calculation of the rate constant k (units l. mole<sup>-1</sup> sec.<sup>-1</sup>). The results are shown in Fig. 4 which is a plot of  $\log_{10}k$ vs. 1/T. The two lines drawn on the figure represent activation energies of (1) 27 and (2) 37 kcal./ mole. The scatter is large so that it is only possible to say that a low activation energy of about 30 kcal./mole is consistent with the experiments.

It did not seem worth while to try to make similar estimates for the hydrocarbons other than acetylene because it is probable that a considerable amount of hydrogenation occurs during the cooling.

## Discussion

These experiments represent an effort to use the new technique of shock wave heating to gain more information about the complex problem of the pyrolysis of hydrocarbons at temperatures over 1500° K. Although the results are crude they form a picture consistent with Porter's<sup>2</sup> proposed acetylene mechanism for the pyrolysis. His scheme involves such reactions as

$$2CH_4 \longrightarrow C_2H_6 + H_2 \tag{1}$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \tag{2}$$

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \tag{3}$$

which provide a simple way for explaining the pyrolysis products we have recovered in our experiments at 1800–1900° K. and 2400–2500° K. (Table III). Porter then suggests a simultaneous polymerization and dehydrogenation process to lead to solid carbon. On the basis of our results which indicate a second-order reaction, an activation energy of about 30 kcal./mole, and mainly  $C_4H_2$  in the products, a particularly likely reaction is

$$2C_2H_2 \longrightarrow C_4H_2 + H_2 \tag{4}$$

with some contribution possible also from

$$2C_2H_2 \longrightarrow C_4H_4 \text{ (vinylacetylene)} \tag{5}$$

although the latter may represent merely a hydrogenation of  $C_4H_2$  as cooling proceeds. As Porter points out these reactions avoid the requirement of free radical intermediates which could arise only from relatively slow processes with much higher activation energies. This is also consistent with the lack of significant effect of NO on the products recovered from  $C_2H_6$  pyrolysis.

Figure 5 shows the variation of the standard free energy of formation with temperature for several hydrocarbons. Except for  $C_4H_2$ , data came from the NBS tables extended as mentioned above.<sup>6</sup> For  $C_4H_2$  we have used a published estimate<sup>5</sup> because the heat of formation does not appear to have been measured. If reaction 4 is not thermoneutral as supposed<sup>6</sup> but actually exothermic due to resonance stabilization of  $C_4H_2$ , it should provide a convenient path for the reaction by delivering part of the heat of reaction in the first step. In general Porter's scheme seems plausible in connection with the free energy values.

It is worth while to consider how our results fit in with previous work of this kind. Blumberg and Frank-Kamenetskii<sup>12</sup> examined the pressure drop in C<sub>2</sub>H<sub>2</sub> heated to about 900° K. at pressures up to 150 mm. and found a decrease consistent with a second-order reaction with a rate constant given by  $k = 4.1 \times 10^{7} e^{-29900/RT}$ l. mole<sup>-1</sup> sec.<sup>-1</sup>. Their activation energy is certainly within our uncertainty. However an extrapolation of his expression to our temperatures gives a rate constant only about 1/20 th of ours. By measuring just the decrease in pressure he would not have noticed reaction 4 but just reaction 5 or further steps beyond these reactions. Therefore it seems quite possible that his actual rate of loss of C<sub>2</sub>H<sub>2</sub> may have been considerably higher.

In a very interesting paper Cole and Minkoff<sup>18</sup> raise objections to Porter's scheme. They observed the concentration of  $C_2H_2$  in diffusion flames of various hydrocarbons by following the absorption of the 729 cm.<sup>-1</sup> band of  $C_2H_2$ . They say that at first sight their results support the  $C_2H_2$  mechanism because acetylene appears in all the flames when the fuel begins to pyrolyze even though the  $O_2$  zone has not been reached. However, they noted less luminosity and less soot in CH<sub>4</sub>-O<sub>2</sub> than in C<sub>3</sub>H<sub>8</sub>-O<sub>2</sub> flames. In fact, the latter compared much more nearly to the heavily sooting flames of  $C_2H_4$ . This comparison seems to be not entirely justified because all the flames were run at constant pressure and equal flow rates of fuel and oxygen. This means that the CH<sub>4</sub> was much hotter and much more nearly completely burned than the higher hydrocarbons. Cole and Minkoff also doubt the  $C_2H_2$  mechanism because they found that 3%  $C_2H_2$  added to the CH<sub>4</sub> greatly increased the amount of absorption at 729 cm.<sup>-1</sup> but did not result in greater luminosity or soot formation. They conclude therefore that other mechanisms must be operating and that  $C_2H_2$  is not a critical intermediate. This point seems to be a valid objection but it would still be interesting to examine flames of other  $CH_4/C_2H_2$  ratios and to try to compare the sooting tendencies of the fuels under fairly standardized conditions of temperature and concentration.

Porter<sup>2</sup> does not consider higher acetylenes as likely intermediates because he says they are too unstable and because no characteristic absorption has been found in his flash photolysis experiments.

(13) D. J. Cole and G. J. Minkoff, Proc. Roy. Soc., London, A239, 280 (1957).

<sup>(12)</sup> D. A. Frank-Kamenetskii, Acta physico. chim. U.R.S.S., **18**, 148 (1943); E. A. Blumberg and D. A. Frank-Kamenetskii, Zhur. Fiz Khim., **20**, 1301 (1946).