

Procedure.—A weighed sample of the disubstituted aminomethyl ether was added dropwise to 15.00 cc. of 1.00 *N* hydrochloric acid which was agitated by means of a mechanical stirrer. An excess of approximately 0.1 *N* sodium bisulfite and 2.0 cc. of starch solution was added and the solution placed in a thermostat. A sufficient amount of a solution of approximately 0.1 *N* iodine was added to use up any ionized sulfite present. When the solution had come to the temperature of the thermostat, the rate was determined by adding successive small portions of iodine solution and noting the time required for the starch color to fade in each case. The total amount of iodine required to reach the permanent end-point was determined by following the reaction to completion. A typical example is given in Table III. This and similar cases are plotted in Figs. 1, 2, 3 and 4.

Summary

The effect of various carbon groups upon the rates of ionization and heats of activation of disubstituted aminomethyl sulfonic acids has been studied.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

THE THERMAL DECOMPOSITION OF METHANE BY A CARBON FILAMENT¹

By H. H. STORCH²

RECEIVED JUNE 20, 1932

PUBLISHED NOVEMBER 5, 1932

The writer has published elsewhere a brief, critical review³ of the literature on the pyrolysis of methane. The thermal decomposition of methane in an isothermal, static system has recently been studied by Kassel⁴ at temperatures low enough (700–850°) so that rate measurements on the early stages of the reaction were feasible. The reaction was found to be a homogeneous one of first order with a heat of activation of about 79,000 calories.

The experiments described in the present paper were all conducted in carbon filament lamps, the objectives being to isolate some of the early products of the pyrolysis of methane by immersing the walls of the bulb in liquid nitrogen or oxygen, and to avoid loss of hydrogen such as occurs in experiments with quartz bulbs. An additional objective was to study the reaction on a carbon surface rather than on quartz or metal surfaces coated with carbon.

¹ Published with the permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Part of this work was presented at the meeting of the American Chemical Society at Buffalo, N. Y., in August, 1931.

² Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

³ "Physical Chemical Properties of Methane," U. S. Bureau of Mines Information Circular 6549, January, 1932.

⁴ L. S. Kassel. *THIS JOURNAL*, **54**, 3949 (1932).

Preparation of Methane and Apparatus

The methane used in the experiments described in this paper was prepared by removal of ethane from Pittsburgh natural gas by adsorption on active charcoal. The gas thus obtained contained 95–98% methane, 2–5% nitrogen, and traces of ethane. The gas was then dried over phosphorus pentoxide, condensed by a bath of liquid nitrogen, and the solid methane repeatedly melted and frozen (the non-condensable gases being pumped off) until a constant vapor pressure (11 millimeters) was obtained. The methane was then allowed to vaporize into an evacuated 5-liter flask, the first and last thirds of the vapor being wasted. Such preparation yielded a gas which contained no detectable quantity of ethane, and only traces of nitrogen.

The reaction vessels consisted of 60-watt, 110-volt carbon filament lamps obtained from the General Electric Company. The filaments are made from cotton peptized with zinc chloride and subsequently washed and carbonized. They averaged 0.18 mm. in diameter and 24 cm. in length. In order to test the possible catalytic activity of the platinized inner leads, a number of specially constructed lamps containing tungsten inner leads were used. The latter gave practically the same results as the ordinary lamp. The lamps were sealed into a system containing an open arm manometer, a Töpler pump, a McLeod gage, a mercury diffusion vacuum pump and a 5-liter reservoir of methane. The mercury levels of the manometer were read with the aid of a Gaertner cathetometer. During the experiments the volume of the carbon filament lamp plus manometer was kept constant with the aid of a mercury leveling bulb attached to the bottom of the manometer.

The filaments were heated by storage battery current, the temperature being measured by a Leeds and Northrup optical pyrometer which had been calibrated by the U. S. Bureau of Standards. The measurement of the temperature by means of the resistance of the carbon filament was found to be impossible due to the variation of the resistance with the character and amount of the gas in the lamp, and to the deposition of small amounts of carbon on the filament.

Isolation of Early Products of the Pyrolysis.—The experiments listed in Table I were all conducted with the lamp completely immersed in a bath of liquid nitrogen contained in a transparent Dewar bulb. Accurate temperature measurements were not possible because of poor visibility through the boiling nitrogen, and hence no attempt was made to take any measurements of the reaction rate, the objective being the isolation of the primary reaction products.

TABLE I
PRIMARY PRODUCTS OF THE DECOMPOSITION OF METHANE BY A CARBON FILAMENT AT 1700°

Expt.	—Pressure measurements—			—Analysis of product, %—				Total time of expt., min.
	Initial with bulb at room temperature, cm.	Final with bulb immersed in liquid nitrogen, cm.	Final with bulb at room temperature, cm.	CH ₄	H ₂	C ₂ H ₆	Unsatd. hydrocarbons	
15	39.29	5.20	41.22	62.6	13.6	20.3	3.4	17
16	33.76	3.52	34.65	55.0	16.4	25.0	3.5	28
17	40.88	3.20	41.74	73.4	11.1	13.8	1.8	14

It will be noted from Table I that the initial and final pressures measured with the bulb at room temperature were only 1 to 2 cm. apart, despite the

2 to 4 cm. (measured at liquid nitrogen temperature and therefore corresponding to 6 to 12 cm. at room temperature) of hydrogen generated. (Note: the vapor pressure of methane at liquid nitrogen temperatures is 1.1 cm. of mercury.) It is apparent therefore from stoichiometric considerations alone that since no carbon or tarry matter was formed, considerable quantities of ethane must have been produced. The gas analyses of Table I are calculated upon the assumption that ethane was the only saturated higher hydrocarbon present. A comparison of the hydrogen content with the percentages of ethane and unsaturated hydrocarbons indicates that the latter are largely ethylene.

The data of Table II were obtained in a manner similar to that of Table I, except that the methane and hydrogen were pumped off while the bulb was still immersed in liquid oxygen or nitrogen. The temperatures were more accurately estimated in these experiments, this being effected by a change in experimental conditions which will be described in a later paragraph.

TABLE II
COMBUSTION RATIOS OF SATURATED HYDROCARBON GAS FORMED IN THE PYROLYSIS OF METHANE BY A CARBON FILAMENT

Expt.	Filament temp., °C.	Cooling liquid around bulb	Analysis of residual gas after removal of CH ₄ + H ₂				Combustion ratio obtained for saturated hydrocarbon
			Absorbed by 1.6 sp. gr. H ₂ SO ₄ , %	Absorbed by K ₂ HgI ₄ , %	Unsaturated hydrocarbons	Satd. hydrocarbons (ethane), %	
49	1700	N ₂	14.4	85.6	1.240
51	2000	N ₂	26.5	73.5	1.270
53	1700	O ₂	50.2	49.8	1.246
60	1700	N ₂	4.2	95.8	1.250
62	1457-1700	O ₂	0.0	8.2	44.6	47.2	1.262
63	1457-1700	O ₂	.3	7.9	38.5	53.3	1.256
64	1457-1570	O ₂	.0	6.4 ^a	14.2	79.4	1.251

^a Absorbed by copper ammonium chloride.

An inspection of the data of Table II shows that the combustion ratios (contraction/carbon dioxide) for the saturated hydrocarbon are reasonably close to the theoretical for ethane, which is 1.250. It should also be noted that the unsaturated hydrocarbons appear to be largely ethylene. No confidence can, however, be placed in the figures for acetylene (absorption by K₂HgI₄), although it is probable that they are not more than 100% in error. Table II also shows that much larger amounts of unsaturates are formed when liquid oxygen instead of nitrogen is used.

Table III shows that very little if any excess hydrogen (and hence no carbon or tars) is produced during the pyrolysis in a bulb immersed in liquid oxygen or nitrogen. The 1.5% excess of experiment 62 is not significant considering the probable inaccuracy of the acetylene figure.

TABLE III

HYDROGEN BALANCE IN THE PYROLYSIS OF METHANE IN A CARBON FILAMENT LAMP
IMMERSED IN LIQUID OXYGEN OR NITROGEN

Expt.	H ₂	Analysis of product calculated on CH ₄ -free basis, %			Hydrogen excess, %	Filament temp., °C.	Cooling liquid around bulb
		C ₂ H ₆	C ₂ H ₄	C ₂ H ₂			
51	54.5	36.5	9.0	Trace	0.0	2000	N ₂
62	60.3	18.8	17.7	3.2	1.5	1570-1700	O ₂

The Order and Heat of Activation of the Decomposition Reaction.—

To determine the effects of the pressure of methane and the filament temperature on the rate of the pyrolysis three series of experiments were made. In the first series the lamp was immersed in liquid oxygen, in the second in a bath of alcohol plus solid carbon dioxide, and in the third in an ice plus water-bath. These will be described in the order mentioned.

Experiments Using Bath at -183° .—It would, at first thought, seem possible to measure the hydrogen pressure due to the decomposition of methane by a carbon filament with the bulb immersed in liquid oxygen, so that all of the products of the reaction other than hydrogen were frozen out. It was, however, found that little change in pressure was obtained when the initial methane pressure was below its saturation value. Ethane, ethylene and acetylene were formed, and since the relative amounts of these varied considerably with the filament temperature and somewhat with the initial pressure of methane, it was not possible to interpret the small pressure changes without an analysis of the products. If an excess of methane was used so that the gas was always at saturation pressure by being in contact with solid methane, it was found that the ethane and ethylene formed during the pyrolysis markedly altered the equilibrium pressure of methane, so that any rate measurements made in the presence of solid methane could not be correlated with a definite pressure of methane.

The procedure finally adopted for the rate measurements may be briefly described as follows.

To the carbon filament lamp previously described was sealed a 15 by 3.8 cm. sight tube, the latter being concentric with the long axis of the lamp. This apparatus was placed in a 14 by 51 cm. Dewar tube, and connected with the rest of the apparatus (manometer, methane reservoir, etc.) by means of 3.2 mm. glass tubing. An optical pyrometer was mounted 25 cm. above the top of the sight tube, the telescope being placed inside a 5-cm. glass tube, the lower end of which was about 2.5 cm. below the top of the sight tube. Since the latter was kept immersed in liquid oxygen to within 1.4 cm. of the top, the 5-cm. tube dipped into the liquid oxygen. In this fashion moisture condensation on the top of the sight tube and on the telescope lens was effectively avoided. The total volume of the lamp plus the connections to the manometer, etc., was 515 cc. Of this volume about 475 cc. was immersed in liquid oxygen, approximately 10 cc. being contained in that portion of the sight tube above the bath level, and the remaining 30 cc. consisted of the volume of the connecting tubes to the rest of the apparatus.

Pure methane was admitted to the previously evacuated reaction vessel. After reading the initial pressure and the barometric pressure, the filament was ignited and

the temperature adjusted to the desired point by varying the resistances in circuit with the filament. The filament was then extinguished and the reaction vessel again evacuated and subsequently refilled with methane to the same pressure as that used to obtain the proper rheostat adjustments for the desired temperature. The filament was then again ignited, the operating pressure measured, and the time interval measured from the moment of ignition of the filament. During most of the time interval the filament was under constant observation and small adjustments of temperature were made when necessary. At the end of the time interval, the filament current was turned off, the final pressure measured, and the mixture of hydrogen and methane pumped off with a Töpler pump, its volume and hydrogen content being subsequently determined. The residual (ethane, ethylene and acetylene) mixture was permitted to accumulate for several experiments before being collected and analyzed. The results are given in Table IV.

TABLE IV
RATE OF DECOMPOSITION OF METHANE IN A CARBON FILAMENT LAMP IMMERSSED IN LIQUID OXYGEN

Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm.			Time of experiment, minutes	Rate of reaction: cc. (at 25° and 74 cm.) of hydrogen per minute	Rate of reaction per cm. of operating pressure × 100
	Initial	Operating	Final			
(a) Temperature, 1700°						
66A	0.50	0.83	0.50	2	0.65	78
66B	0.74	1.24	0.74	2	.95	77
65A	2.38	5.38	2.42	2	4.35	81
63C	3.24	6.34	3.31	3	5.40	85
62B	3.33	6.54	3.23	3	5.60	86
65B	4.29	8.80	4.55	2	7.75	88
65C	6.31	11.20	7.16	2	13.10	117
63G	6.01	11.59	7.44	2	26.80	231
66C	6.40	14.00	7.90	2	49.50	354
66D	6.21	16.85	9.15	2	50.50	300
66E	8.43	23.63	13.03	2	92.75	394
(b) Temperature, 1570°						
63A	1.20	1.75	0.97	10	0.36	20.6
64A	1.20	2.10	1.18	5	.48	22.8
63B	3.37	6.43	3.26	5	2.98	41.4
62G	3.26	6.50	3.32	10	2.60	40.0
64C	5.37	8.57	5.41	2	3.85	45.0
64D	6.46	9.59	6.59	2	5.40	57.0
(c) Temperature, 1457°						
64F	1.14	1.64	0.94	60	0.10	6.1
65D	2.28	4.22	2.32	20	.225	5.3
64E	3.13	6.35	3.17	10	.32	5.0
65E	4.28	7.30	4.48	10	.605	8.3
63H	6.12	8.32	6.08	20	.66	7.9

Before discussing the data of Table IV, it is desirable to indicate the composition of the higher hydrocarbons produced in the pyrolysis at various temperatures. This is done in Table IVd.

TABLE IVd

COMPOSITION OF HIGHER HYDROCARBONS PRODUCED IN THE PYROLYSIS OF METHANE BY
A CARBON FILAMENT LAMP IMMERSSED IN LIQUID OXYGEN

Temp. range, °C.	Operating pressure range, cm.	Average composition of hydrocarbon products, %			
		C ₂ H ₂	C ₂ H ₄	Higher olefins	C ₂ H ₆
1700	1-9	38.4	35.3	1.1	25.2
1700	11-23	68.7	25.7	0.9	4.7
1457-1500	2-10	6.4	14.2	...	79.4

In considering the data of Table IVa it should be noted that the rate constants for operating pressures greater than 9 cm. are not directly comparable with the others, for almost twice as much acetylene was produced in the 11-23 cm. range as in the 1-9 cm. The figures for the 11-23 cm. range should be divided by the factor 1.34 in order to be comparable with those for the lower pressures. This correction, however, does not affect materially the general trend of the constants, which indicate a first-order reaction in the low-pressure range, but this increases to almost second order in the 11-23 cm. range. The data of Tables IVb and IVc indicate an increase in the order of the reaction with increasing pressure.

With regard to the heat of activation of the reaction, the results at 1457 and 1570° are comparable, but neither of these are directly comparable with the 1700° data. The latter, in the 1-9 cm. pressure range, indicate that about 1.7 times as much hydrogen per mole of methane reacted was produced as compared with the 1457-1570° results. The data on the heats of activation are summarized in a later section which includes similar calculations from the data of Tables V and VI where solid carbon dioxide plus alcohol and ice plus water, respectively, were the cooling agents.

Experiments Using Bath at -78°.—In the experiments of Table V a mixture of ethyl alcohol and solid carbon dioxide was used as the cooling bath. Because of the frothing of this mixture it was found necessary to seal the 5-cm. tube containing the pyrometer telescope onto the 3.8-cm. sight tube of the reaction vessel with paraffin in order to maintain clear visibility. Since the reaction under these conditions proceeds almost completely to carbon and hydrogen, pressure measurements were a reliable index of the rate.

Table V also indicates a first-order reaction at the lower pressures with an increase toward second order at the higher pressures. In order to compare the rates of Table V with those of Table IV the pressure increases per minute per cm. operating pressure of Table V must be multiplied by a factor which will convert these pressure increases to cc. of hydrogen at 25° and 74 cm. pressure, and which will also take care of the differences in character of the products of Table IV as compared with Table V. This factor for the 1700° data of Table V is 11.3 for comparison with the 1-9 cm. range of Table IV, and 14.0 for comparison with the 11-23 cm. range. The

TABLE V
 RATE OF DECOMPOSITION OF METHANE IN A CARBON FILAMENT LAMP IMMERSSED IN AN
 ALCOHOL PLUS SOLID CARBON DIOXIDE BATH
 Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm.			Time of expt., minutes	Pressure increase per minute	Pressure increases/min per cm. Initial × 100	Pressure increases/min per cm. Operating × 100
(a) Temperature, 1700°							
67A	1.51	2.20	1.87	3	0.120	7.96	5.47
67B	2.49	3.75	2.94	2	.225	9.03	6.00
67C	4.67	6.90	5.40	2	.365	7.80	5.27
67D	4.19	7.07	5.13	2	.470	11.17	6.12
67E	9.03	14.81	10.95	2	.960	10.65	6.50
67F	8.63	14.83	11.00	2	1.185	13.75	7.98
67G	16.64	32.47	22.81	2	3.085	18.53	9.50
(b) Temperature, 1570°							
68A	0.76	0.99	0.90	10	0.014	1.84	1.42
68B	1.86	2.50	2.01	5	.030	1.61	1.20
68C	2.08	2.93	2.23	5	.030	1.44	1.02
68D	2.28	3.20	2.43	5	.032	1.40	1.00
68E	4.36	6.07	4.68	5	.064	1.47	1.05
68F	4.30	6.20	4.70	5	.080	1.85	1.28
68G	8.80	13.75	9.89	5	.218	2.48	1.58
68H	16.33	26.95	19.49	5	.632	3.87	2.34
68I	33.66	55.51	39.37	2	2.855	8.45	5.13
(c) Temperature, 1457°							
69A	4.02	5.74	6.04	15	0.020	0.50	0.35
69B	8.47	13.03	9.13	15	.044	.52	.34
69C	8.87	13.45	9.52	15	.043	.49	.32
69D	16.36	26.27	17.43	5	.214	1.31	.80
69E	33.01	52.82	37.77	5	.952	2.88	1.80

factor for the 1457 and 1570° data of Table V is 6.7. Using these factors one notes that the 1457 and 1570° rates of Table V are 3 to 5 times smaller than those of Table IV, and that there is approximate agreement at 1700° in the 1-9 cm. range, whereas the rates of the 11-23 cm. range of Table V are smaller by a factor of about two. If, however, one compares operating concentrations instead of operating pressures of methane these differences are reduced by a factor of about 2.2, which results in fair agreement for the 1457° and the 11-23 cm. range at 1700° rates of the two tables. The 1-9 cm. rates at 1700° of Table V are now about 60% higher, and the 1570° rates about 50% smaller than those of Table IV. These differences are, however, within the limits of reproducibility of the data, and one can therefore say that there is approximate agreement between the rates of the pyrolysis of methane when conducted so that the primary products are rapidly removed and when the latter are permitted to react further so as to produce mainly carbon and hydrogen. This point is of considerable

importance for the agreement, although only approximate, indicates that the secondary reactions which ethane initiates are of minor importance in controlling the rate of the reaction in the presence of only small amounts of hydrogen. A later section will show that the secondary reactions become important when appreciable quantities of hydrogen are present.

Experiments with Bath at 0°.—The procedure and apparatus used with ice plus water as the fluid surrounding the reaction vessel were identical with those for liquid oxygen. The products of the reaction with the 0° bath were largely carbon and hydrogen. The results are given in Table VI.

TABLE VI
RATE OF DECOMPOSITION OF METHANE BY A CARBON FILAMENT LAMP IMMERSSED IN AN
ICE PLUS WATER BATH
Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm.			Time of expt., minutes	Pressure increase per minute	Pressure increases per minute	
	Initial	Operating	Final			per cm. Initial × 100	per cm. Operating × 100
(a) Temperature, 1700°							
70A	2.19	2.95	2.70	2	0.255	11.65	8.65
70B	4.27	5.97	5.15	2	.440	10.30	7.38
70C	4.37	6.07	5.40	2	.515	11.78	8.48
70D	8.32	12.25	10.95	2	1.315	15.80	10.73
(b) Temperature, 1570°							
71A	1.56	2.02	1.80	5	0.048	3.08	2.37
71B	4.42	5.89	4.92	5	.10	2.26	1.70
71C	8.46	11.51	9.41	5	.19	2.25	1.65
71D	16.89	24.32	19.74	5	.57	3.38	2.34
71E	33.25	50.20	40.50	2	3.625	10.9	7.22
(c) Temperature, 1457°							
72A	4.29	5.41	4.51	15	0.015	0.350	0.277
72B	4.26	5.51	4.54	15	.019	.446	.345
72C	8.61	11.22	9.07	15	.031	.360	.276
72D	16.40	21.93	16.76	5	.072	.433	.324
72E	33.62	45.36	36.27	5	.530	1.575	1.462

The data of Table VI also indicate a first-order reaction at the lower pressures, and an increase toward second order at the higher pressures. Upon comparing Tables V and VI it will be noted that there is fair (within about 25%) agreement at 1700 and 1457°, and at 1570° in the 11–50 cm. operating pressure range, whereas in the 2–6 cm. range the rates of Table VI are about twice those of Table V. If operating concentrations instead of pressures are compared (the factor between 0 and –78° is 1.4), the agreement is generally poorer, but except for the 2–6 cm. range at 1570° the rates agree within a factor of about 2.

Heat of Activation of the Reaction.—In order to facilitate the calculation of the heat of activation the rate data were plotted against the operat-

ing pressures using the data of Tables IV, V and VI. Extrapolation of the curves to very low pressures yielded the data given in Table VII. It should be noted that the 1700° rate resulting from the extrapolation of the data of Table IV must be divided by 1.7 so as to make this datum comparable with the rates at 1457 and 1570°. The nine heats of activation calculated from the extrapolated rate constants are also presented in Table VII.

TABLE VII

(A) EXTRAPOLATED RATE CONSTANTS $\times 100$			
Temp., °C.	Extrapolation of data from Table no.		
	4	5	6
1700	76.5/1.7	5.7	8.2
1570	22.0	1.1	1.8
1457	5.0	0.4	0.27

(B) HEATS OF ACTIVATION			
Temp. intervals, °C.	Calories per mole of methane		
	4	5	6
1700-1570	40,900	91,350	84,050
1570-1457	83,000	56,700	108,000
1700-1457	60,750	74,050	95,700
Averages	61,550	74,030	95,920

There appears to be a trend in the heat of activation in going from the liquid oxygen bath to the solid carbon dioxide plus alcohol and ice plus water baths. It is difficult to see any reason for expecting such a change in the heat of activation in view of the approximate agreement (within a factor of about two) of the rates of Tables IV, V and VI. Hence the writer is disposed to average all of the values of Table VII for the heat of activation. This yields 77,170 calories with an average deviation of 16,950 calories from the mean. The probable error of the mean is about 10,000 calories, and hence the heat of activation may be written as $77,170 \pm 10,000$ calories.

Effect of Hydrogen on the Rate.—If one accepts the mechanism of the thermal decomposition suggested by L. S. Kassel,⁴ namely



then the equation for the rate of generation of hydrogen is

$$\frac{d(\text{H}_2)}{dt} = \frac{a(\text{CH}_4)^2}{b(\text{CH}_4) + c(\text{H}_2) + d(\text{H}_2)^2 + e(\text{H}_2)^3} \quad (6)$$

where a , b , c , d and e are constants. Hence for experiments at constant pressure of methane, the rate at very low concentrations of hydrogen reduces to

$$\frac{d(\text{H}_2)}{dt} = \frac{K}{K' + K''(\text{H})^2} \quad (7)$$

At higher pressures of hydrogen the square and cube of the hydrogen pressure will be the important terms in the denominator of equation (6).

Equation (7) indicates that a straight line should be obtained when the reciprocal of the rate of hydrogen generation at constant methane pressure is plotted against the hydrogen concentration. Such a straight line should extend for a distance corresponding to small values of (H_2) . For higher values of the hydrogen concentration, equation (6) indicates that the curve should bend fairly sharply toward the axis on which the reciprocal of the rate is measured.

In Expts. 33 and 34 the methane pressure was held constant by attaching a small (10-cc.) bulb to a carbon filament lamp⁵ and keeping the bulb immersed in liquid nitrogen. The lamp itself was at room temperature when the pressure readings were made at the end of each time interval. The 10-cc. bulb was several cm. off to one side of the lamp so that the cold nitrogen gas did not affect the temperature of the former appreciably. Under these conditions the products of the reaction were mainly carbon and hydrogen. The results are listed in Table VIII. The total volume of the reaction system in these experiments was 270 cc. and the room temperature $22 \pm 3^\circ$ (corrections were made for fluctuations in room temperature during each experiment).

TABLE VIII
DATA CONCERNING EFFECT OF HYDROGEN ON RATE
Total volume of reaction vessel, 270 cc.

Experiment No. 33 Temperature, 1570°		Experiment No. 34 Temperature, 1800°	
Pressure of hydrogen, cm.	Rate of pressure increase, cm./min.	Pressure of hydrogen, cm.	Rate of pressure increase cm./min.
0.06	0.02	0.085	0.17
.19	.014	.24	.13
.33	.014	.36	.12
.66	.009	.49	.07
1.15	.008	.68	.05
1.52	.0056	.92	.044
1.68	.0047	1.13	.038
1.82	.0040	1.38	.031
		1.67	.028
		2.01	.021
		2.48	.014

A plot of the data of Table VIII indicates that the data up to about 1 cm. pressure of hydrogen ($H_2/CH_4 =$ about 0.9) do seem to form a straight line and that the curve swings upward very rapidly when the H_2/CH_4 ratio becomes greater than unity.

⁵ Rate measurements with appreciable amounts of hydrogen present could not be made with the lamp completely immersed in liquid nitrogen, because the conduction of heat by the hydrogen raised the temperature of the solids (CH_4 , C_2H_6 , C_2H_4) and made the pressure of CH_4 uncertain.

Discussion

The increase in the apparent order of the decomposition of methane from first to about second with increase in methane pressure beyond about 8 cm. may conceivably be due to a large change in the temperature gradient in the immediate vicinity of the hot filament. Unfortunately it does not seem possible to obtain unequivocal criticisms of this possibility by a mathematical analysis of the flow of heat from the filament at various pressures of methane. The rate measurements made at pressures higher than about 8 cm. are generally not reproducible, whereas those below that pressure are readily reproduced within a factor of about 2.

The mechanism suggested by L. S. Kassel⁴ accounts satisfactorily for the first order of the reaction when measurements are made at low concentrations of hydrogen and approximately constant $(\text{H}_2)/(\text{CH}_4)$ ratio, which is true of the data given in Tables IV, V and VI at methane pressures less than about 8 cm. This mechanism also predicts the shape of the curves obtained by plotting the data of Table VIII for the effect of hydrogen pressures on the rate.

Summary

The earliest product of the thermal decomposition of methane which has been isolated is shown to be ethane. In one experiment as much as 95% of the theoretical yield of ethane was obtained, by the decomposition of methane in a carbon filament lamp immersed in liquid nitrogen.

The thermal decomposition of methane by a carbon filament was found to be a first-order reaction at methane pressures from 1 to about 8 cm., the heat of activation being $77,170 \pm 10,000$ calories per mole. Above 8 cm. methane pressure the order increases to about second. Since no such increase is observed in isothermal static experiments, it seems probable that the increase is due to a rapid change in the temperature gradient in the immediate vicinity of the filament.

The influence of hydrogen on the rate of the decomposition was studied and the data obtained can be satisfactorily explained by a rate equation (derived by L. S. Kassel) based on a number of successive dehydrogenation steps following the initial synthesis of ethane.

PITTSBURGH, PENNSYLVANIA