

4. The hydrolysis of these substances, which served as the basis for the elementary analysis, is discussed. The resemblance of these compounds to the analogous compounds of carbon, as is to be expected, is for the most part merely a matter of similarity in formula.

CAMBRIDGE, MASSACHUSETTS

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

THE THERMAL DECOMPOSITION OF METHANE¹

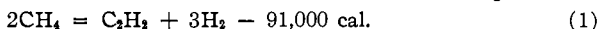
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Introduction

The thermal decomposition of methane has been repeatedly studied, but none of the results obtained has been of much value from the standpoint of reaction kinetics. The only previous work which need be considered here is that of Holliday and his co-workers.³ It was found that the earlier stages of the reaction, at 900–1200°, were homogeneous in silica vessels; the reaction is retarded very greatly by the hydrogen produced, and the final slow stages of the decomposition are at least partly heterogeneous. It is a practical impossibility to attain equilibrium without a catalyst; the "false equilibrium" which is reached from the methane side is characterized by a "constant," $(\text{CH}_4)^2/(\text{H}_2)^3$; the temperature coefficient of this constant corresponds to a heat term of 72,000 cal. Holliday worked only at temperatures where the first few per cent. of decomposition occurred too rapidly for measurement in static systems; nevertheless, Holliday and Gooderham decided that the initial reaction was the bimolecular process



They gave two reasons for this proposal; the first of these was the rather surprising statement that "homogeneous, unimolecular reactions are rare, and a bimolecular process is much more probable than one of higher order";⁴

¹ Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) A portion of this work was presented at the New Orleans meeting of the American Chemical Society, March, 1932.

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³ Holliday and Exell, *J. Chem. Soc.*, 1066 (1929); Holliday and Gooderham, *ibid.*, 1594 (1931).

⁴ Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, 1932, lists 20 reactions which are probably unimolecular, seven which may be bimolecular, excluding the large group of bimolecular reactions which involve free atoms; of these seven, four involve the participation of two different substances, and hence could not be expected to be unimolecular. From the available statistical data, therefore, the odds are 20 to 3 that the initial step in the decomposition of a gaseous substance will be unimolecular.

and second, the slightly greater percentage decomposition obtained at higher pressures during the earlier stages of the decomposition.⁵ It is easy to see that (1) is at best a very unlikely first step. At 912° and 500 mm. pressure, the initial rate of decomposition estimated from the curves given by Holliday and Gooderham is 1.5 mm./sec.; the corresponding second order rate constant is 6×10^{-5} mm.⁻¹ sec.⁻¹, or 4.8×10^3 cc. mole⁻¹ sec.⁻¹. It is safe to assume that the rate constant of (1) will not exceed $10^{14}e^{-E/RT}$ cc. mole⁻¹ sec.⁻¹, where E is its energy of activation; the minimum value possible for E is the negative of the heat of reaction; at 912° this would not differ significantly from the 91,000 cal., which is correct at room temperature. The maximum rate to be expected at 912° for a reaction with an energy of activation of 91,000 cal. is 3×10^{-2} cc. mole⁻¹ sec.⁻¹, or about 10^{-5} the observed value. To give a sufficiently rapid bimolecular reaction, an energy of activation not greater than 61,000 cal. would be needed. This might conceivably have been possible for



or



but it will be shown clearly in what follows that these reactions do not occur to an appreciable extent.

The experiments to be reported here were designed to unravel as completely as possible the complex kinetic behavior of methane decomposition in static systems. They constitute part of a larger program in progress at this station, the goal of which is the more efficient utilization of natural gas. A subsequent paper by Storch,⁶ to which reference will be made later, reports on another phase of this investigation.

Experimental Method

Two electric furnaces were used in this work; the first of these was wound with platinum wire on an alundum core which contained the reaction vessel, a long clear quartz tube of 1 or 2 cm. diameter. The temperature was regulated by a Leeds-Northrup controlling potentiometer used in conjunction with a platinum-platinum-rhodium thermocouple in contact with the reaction vessel. The second furnace was wound with nichrome ribbon on a large alundum core, 10 cm. in diameter; it could hold a reaction vessel of 500 cc. capacity. In both furnaces there were temperature gradients along the axis; for the longer tubes used in the platinum-wound furnace, the extreme temperature differences may have reached 10°; hence, the temperature of the thermocouple is not strictly the average temperature of the reaction vessel, and the temperatures measured in different series are not quite comparable.

In almost all of the work the reaction was followed by measurement of the pressure change. Under the experimental conditions adopted, the only products of importance are carbon and hydrogen, as will be clearly shown later; traces of oily material condense in the capillary leading to the manometer, chiefly in the region which is at approximately

⁵ In the experiments being reported here, this relation was not confirmed.

⁶ Storch, *THIS JOURNAL*, in press.

100°, but their quantity is negligibly small. Hence the pressure increase is a direct measure of the amount of reaction. In view of the small volume of the reaction vessel used in part of the work, and of the high temperature of the reaction zone, a small outside volume was essential. In some of the earliest experiments this was achieved by using a capillary manometer; later a click gage, built with the smallest possible bulb, was used; the clicking pressure was then read with a cathetometer on a wide-bore manometer filled with either mercury or α -bromonaphthalene; the results obtained in this way were far more satisfactory. When a larger reaction vessel was used, the click gage was unnecessary. In all cases, a correction for the outside volume was made in the usual manner.

Throughout the work the loss of hydrogen by diffusion through the quartz was a source of difficulty. The order of magnitude of this loss is about 1% per hour, depending upon the surface-volume ratio of the vessel, the wall thickness, possibly the extent of devitrification; between 700 and 1050° the rate about triples. Over a considerable range of pressure, at least from 1 to 50 cm., the rate of diffusion is proportional to the hydrogen pressure. In some of the experiments a double-jacketed reaction vessel was used, the hydrogen which diffused through the inner wall being caught in the outer annular space, and its pressure read on a McLeod gage; since only a few per cent. of this hydrogen remained within the hot zone, the loss by secondary diffusion was entirely negligible. This method failed at such pressures that the primary diffusion was about ten times the reaction rate, it being no longer possible to attain accuracy in the pressure measurements sufficient to permit calculation by difference of the small pressure change due to reaction. Since knowledge of the rate in this region is of considerable importance to a complete understanding of the reaction mechanism, experiments were tried also with sillimanite tubes. These proved slightly less permeable than quartz, possibly because of their greater thickness; the difference was not sufficient to compensate for the practical impossibility of constructing a double-jacketed reaction vessel.

The occurrence of an induction period, as will be described later, suggested that appreciable quantities of ethane or ethylene (*ca.* 5 mm.) might be present during the middle stage of the reaction. An attempt to isolate these substances was therefore made. A large bulb immersed in liquid nitrogen was connected by a stopcock to the reaction vessel; methane was admitted to the former, allowed to decompose for a few minutes, and then frozen out in the cold bulb; the products of about 25 runs were collected, the methane removed by cautious pumping until a pressure of about 0.5 mm. was reached, and the residue warmed to room temperature. The quantity of gas obtained was far too small for analysis, corresponding to a pressure in the reaction vessel of about 0.1 mm. per run.

The methane used was prepared from Pittsburgh natural gas by removing the ethane with active charcoal; the product analyzed 97% or more of methane, the remainder being almost entirely nitrogen; this material was further purified in the apparatus by liquefaction and repeated pumping until the vapor pressure at liquid nitrogen temperature had become constant; after about 75% of the resulting material had been used, the remainder was ordinarily discarded, but no difference in rate was found when this was not done. The purity of the final product probably exceeded 99.9%.

Experimental Results

The Induction Period.—Under some conditions an induction period was observed, the nature of which remains obscure. A typical pressure-time curve showing this induction period is reproduced in Figure 1. The difference between the measured initial pressure and that extrapolated from the straight line part of such curves varied from 1 or 2 mm. up to

1 cm. The general tendency was toward longer and more intense induction periods at low pressures and in bulbs free from carbon; in the packed bulb, where the surface-volume ratio was highest, no induction period was observed. In some other series of experiments, also, it was absent; within any single series it behaved in a fairly uniform way, but results could not be exactly reproduced. The possibility that the induction period might represent the accumulation of steady-state concentrations of higher hydrocarbons suggested the attempts to isolate ethane and ethylene, with the negative result already described.

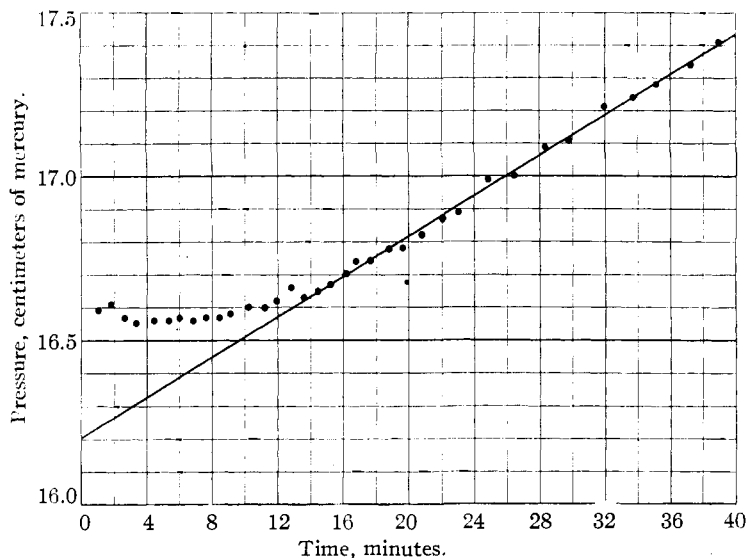


Fig. 1.—Run E29: typical induction period.

Homogeneity.—The homogeneity of the initial reactions at the lower temperatures of the present work could not be assumed to be proved by the experiments of Holliday and Gooderham; accordingly, measurements were made with a clear quartz flask of 415 cc. capacity, and with the same flask packed with short lengths of clear quartz tubing, the free volume then being 280 cc. For the empty flask the surface-volume ratio was 0.65 cm^{-1} , and with the packing it was at least 13 cm^{-1} . The results are shown in Table I. Due to an oversight, the somewhat high rate obtained in the single run made with the packed bulb free from carbon was not noticed in time to run a duplicate. Even if this high value is correct, only 3% of the rate in the empty, clean bulb would be due to surface reaction. In the carbon-coated bulb, the possible contribution of a wall reaction during the initial stages is less than 1%. Hydrogen disappeared in the packed bulb at the rate of 6% per hour. This was sufficiently small so that no appreciable error was caused in pressure readings during the

first fifteen minutes, which is the period used in the experiments of Table I. The justification for using first-order rate constants is contained in the next paragraph.

TABLE I
INITIAL RATE OF DECOMPOSITION IN PACKED AND UNPACKED BULBS, AT 800°

Run no.	State of bulb	Initial press., cm.	k , sec. ⁻¹
F17	Empty, clean	24.5	4.36×10^{-5}
F18	Empty, carbon	15.1	5.71
F19	Empty, carbon	24.5	6.55
F20	Empty, clean	25.2	5.67
F21	Empty, carbon	24.5	5.14
F22	Empty, carbon	24.5	6.10
F23	Empty, carbon	25.4	6.14
F24	Packed, clean	26.6	8.47
F25	Packed, carbon	26.6	4.84
F26	Packed, carbon	25.1	5.13
F27	Packed, carbon	15.8	6.08
F28	Packed, carbon	38.5	5.45
Average	Packed, carbon		5.37
Average	Empty, carbon		5.93
Average	Packed, clean (1 run)		8.47
Average	Empty, clean		5.01
Average	Packed, all runs		6.00
Average	Empty, all runs		5.67

Order.—All of the results which provided any test of the order of the reaction during the first few per cent. of decomposition showed that it was of the first order. The most extensive study of this point is that recorded in Table II. These experiments were made in a long quartz tube, using a click gage and, at the lower pressures, an α -bromonaphthalene manometer. The constancy of the first-order rate constants is all that could be desired. The pronounced retardation by hydrogen makes it utterly impossible to calculate first-order rate constants during a single run; the variation of initial rate with initial pressure, however, is in any case the only trustworthy criterion of order.

The series of experiments reported in Table II is one of those in which no induction period was observed. When induction periods did occur, the first-

TABLE II
FIRST ORDER CONSTANTS BASED ON THE INITIAL RATES AT 735°

Run no.	Initial press., cm.	k , sec. ⁻¹
B2	1.30	1.19×10^{-5}
B3	2.44	1.06
B4	2.60	1.40
B5	4.75	1.13
B6	11.18	1.21
B7	16.47	1.03
B8	29.64	1.14

TABLE III
TEMPERATURE DEPENDENCE OF THE FIRST ORDER CONSTANTS FOR THE INITIAL RATE

T, °C.	$k \times 10^6$ (sec. ⁻¹)		Number of runs
	Obs.	Calcd.	
976	1.31	1.2	3
1008	4.30	4.5	9
1061	32.5	32	2
1113	192	190	3

The calculated values are derived from the equation $\log k = 11.864 - 17,352/T$, or $k = 7.3 \times 10^{11} e^{-79385/RT}$.

order constants were calculated from the straight line part of the pressure-time curve. The constants so obtained were very consistent and showed absolutely no dependence upon the amount of carbon initially present.

Temperature Coefficient of the Initial Reaction.—The temperature coefficient of the initial reaction may be determined from the data of Table III. The absolute rates of this table are low for two reasons: first, they have not been corrected for the outside volume, and, second, they are based on rather too great an extent of reaction, so that the hydrogen retardation has reduced them; the possible error in the energy of activation may be estimated as 6000 cal. The rate constant for the initial period of the reaction may be rounded off and written

$$k = 1.0 \times 10^{12} e^{-79385/RT} \text{ sec.}^{-1}$$

with an uncertainty in absolute value of a factor of about 2. It may be noted that this equation for the initial rate is apparently capable of extrapolation even to 1500°. This is shown by Table IV, which is based on rates estimated from curves given by Holliday and Gooderham, and computed from percentage conversions given by Rudder and Biedermann.⁷ The results of these latter workers scatter rather badly; only those experiments have been considered in which the percentage conversions are comparatively low; in many cases the longer contact time gave the smaller

TABLE IV
COMPARISON OF INITIAL RATES FOUND BY HOLLIDAY AND GOODERHAM AND BY RUDDER AND BIEDERMANN WITH VALUES EXTRAPOLATED FROM THE DATA OF TABLE III

T, °C.	Observer	($k_{\text{obs. sec.}^{-1}}$)	($k_{\text{calcd. sec.}^{-1}}$)
1173	R + B	0.0009 to 0.014	0.0016
1185	H + G	.0030	.0023
1273	R + B	0.018 to .057	.023
1286	H + G	.08	.03
1473	R + B	0.14 to .25	1.7
1573	R + B	1.0 to 4.5	9.3
1673	R + B	10 to 26	43
1773	R + B	50	160

Rudder and Biedermann's conversions at 1473°K. are all far too low and must be disregarded.

⁷ Rudder and Biedermann, *Bull. soc. chim.*, **47**, 704 (1930).

conversion, and hence the variation in k represents experimental error and not any perturbation due to hydrogen retardation. The rate at 1500° is about 10^6 times the highest rate measured in the present experiments; if the extrapolated rate at that temperature is wrong, even by a factor of 4, this could be explained by an error in the temperature coefficient of only 8000 cal. The comparisons of Table IV, in spite of their approximate character, furnish evidence that the initial rate determining steps remain the same over the entire temperature range from 700 to 1500° .

Dependence of the Rate on Hydrogen Concentration.—As has already been stated, it was a matter of considerable difficulty to get accurate measurements when the hydrogen pressure was large because the rate became very small and at the same time the rate of loss of hydrogen increased. Table V contains the data for one of the few successful experiments made. The constancy of the values in the columns headed K and K' is to be used in a later section as evidence for the essential correctness of the mechanism there proposed. Other runs also give constant values for K' and, after sufficient hydrogen has accumulated, for K also. With an initial methane pressure of about 25 cm., K' is rather less, being perhaps as low as 0.02; the significance of this will be considered later.

TABLE V
HYDROGEN DEPENDENCE OF THE RATE AT 760° , RUN NO. C 1

CH ₄ , cm.	H ₂ , cm.	-(dCH ₄ /dt), cm./min.	K	K'
8.05	0.85	0.0450		0.045
7.39	2.16	.0348		.044
6.59	3.75	.0374	0.045	.091
6.06	4.81	.0133	.040	.058
5.72	5.47	.0130	.065	.084
5.38	6.11	.00668	.053	.063
5.44	6.72	.00513	.061	.069
4.73	7.24	.00343	.058	.064
4.41	7.75	.00285	.068	.073
4.07	8.21	.00178	.060	.063
3.81	8.48	.00113	.047	.050
3.51	8.51	.000435	.022	.023
2.83	8.87	.00124	.11	.11
2.28	8.92	.000248	.034	.035

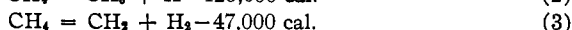
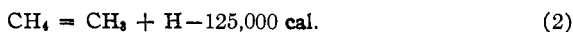
The values in the columns headed K and K' are given by

$$K = \frac{[\text{H}_2]^3}{[\text{CH}_4]^2} \left(- \frac{d[\text{CH}_4]}{dt} \right)$$

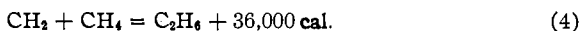
$$K' = \frac{[\text{H}_2]^3 + 8[\text{CH}_4]}{[\text{CH}_4]^2} \left(- \frac{d[\text{CH}_4]}{dt} \right)$$

Discussion and Conclusions

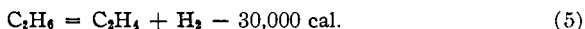
There appears to be no possibility, and no necessity, of considering any primary process except the unimolecular dissociation of methane. This might conceivably take place in two ways



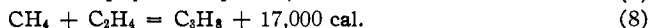
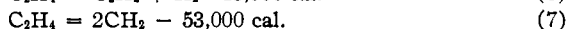
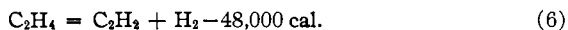
Comparison of the heats of these reactions, which unfortunately are but crude estimates, with the experimental heat of activation provides good reason for favoring (3). At the start of the reaction, CH_2 will of necessity react with CH_4 ; it will not dissociate further, since it is physically stable; it will not recombine with H_2 , which is present at too low a concentration, and for a similar reason it will not polymerize to ethylene. The product of the reaction between CH_2 and CH_4 might *a priori* have been predicted as either ethane or ethylene; the lamp bulb experiments of Storch⁶ show that under suitable conditions 95% of the decomposed methane can be recovered as ethane; we therefore write as the next step



It may be well to point out that this reaction could perfectly well be bimolecular as written; it is only in the case of quite simple molecules that a bimolecular association reaction is subject to difficulties.⁸ The next step is one to which no uncertainty attaches. Long ago, Bone and Coward⁹ showed that at 675° ethane dissociates rapidly, the first products being ethylene and hydrogen; hence we write



There is abundant evidence from later work that (5) is a first order reaction. The pyrolysis of ethylene at temperatures of 700° and higher yields a complex group of products, including hydrogen, methane, ethane, small amounts of acetylene and varying quantities of heavier hydrocarbons. At the low partial pressure of ethylene encountered in the present experiments, the polymerization reactions will no longer be of importance. There are then these possibilities



The process (8) is somewhat analogous to (4); it may take place to some extent but under the conditions prevailing in these experiments it is probably not of major importance; (7) can be made to account for the products obtained in ethylene pyrolysis only with the help of such postulated reactions as



it being supposed then that CH polymerizes to acetylene, and that CH_2 and C_2H_4 are hydrogenated to methane and ethane, respectively. This picture is found repeatedly in the literature; it suffers from the serious difficulty that the hydrogen atoms in CH_2 are probably bound much more

⁸ Kassel, *THIS JOURNAL*, 53, 2143 (1931).

⁹ Bone and Coward, *J. Chem. Soc.*, 93, 1197 (1908).

firmly than those in methane,¹⁰ and that as a consequence CH₂ would decompose far more slowly than methane; it would then be impossible to obtain the high yields of methane which have been repeatedly observed. Any CH₂ formed by (7) during the initial pyrolysis of ethylene would probably give propylene

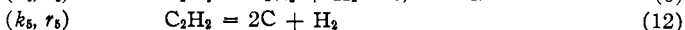
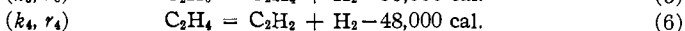
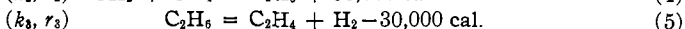
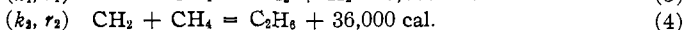
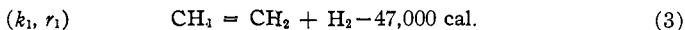


This substance was actually found in significant quantities by Frey and Smith¹¹ as an early product of the pyrolysis of ethylene at 575°; it was accompanied, however, by comparable quantities of methane, ethane and hydrogen. These latter products can most naturally be accounted for by (6), followed by the reversed reactions (5), (4) and (3). It will be considered here that (6) is the only mode of decomposition of the ethylene; (7) may quite possibly occur also, but to consider both would complicate the scheme unwarrantedly. It will be supposed also that the acetylene decomposes simply to carbon and hydrogen



This reaction may be wholly or in part heterogeneous. In support of (12) there may be noted the fact that at 1000° and above, where polymerization has become unimportant, the chief products of acetylene pyrolysis are carbon, hydrogen and methane. At the low partial pressures of acetylene in the present experiments, polymerization would never have much chance to occur. The methane is presumably formed by the reversed reactions (6), (5), (4) and (3).

This scheme of reactions, which has been formulated almost entirely independently of the observed kinetics of methane composition, is surprisingly successful in accounting for these kinetics. The reactions and the rate constants which will be used for them are as follows (k is the constant for a reaction as written, r for the reverse reaction)



The consequences of this scheme may be deduced by the usual steady-state method; the concentrations of CH₂, C₂H₆, C₂H₄ and C₂H₂ are all small compared to those of H₂ and CH₄, and hence their rates of change may be set equal to zero. The four resulting equations may be solved to give these four concentrations; the rate of decomposition of the methane is $-(d[\text{CH}_4]/dt) = 2(k_5[\text{C}_2\text{H}_2] - r_5[\text{H}_2])$

$$= 2 \frac{k_1 k_2 k_3 k_4 k_5 [\text{CH}_4]^2 - r_1 r_2 r_3 r_4 r_5 [\text{H}_2]^4}{r_1 r_2 r_3 r_4 [\text{H}_2]^3 + r_1 r_2 r_3 k_5 [\text{H}_2]^2 + r_1 (r_2 + k_3) k_4 k_5 [\text{H}_2] + k_2 k_3 k_4 k_5 [\text{CH}_4]}$$

¹⁰ The best value available is CH₂ = C (gaseous) + H₂ - 124,000 cal. as compared with CH₄ = CH₂ + H₂ - 47,000 cal.

¹¹ Frey and Smith, *Ind. Eng. Chem.*, 20, 948 (1928).

It is evident that, at equilibrium

$$\frac{k_1 k_2 k_3 k_4 k_5}{r_1 r_2 r_3 r_4 r_5} = \frac{[\text{H}_2]^4}{[\text{CH}_4]^2}$$

The best available free energy equation for the formation of methane is probably

$$\Delta F = -15,313 + 10.54T \ln T - 4.36 \times 10^{-3} T^2 - 0.11 \times 10^{-6} T^3 - 48.56T$$

This is based on the equation given by Storch,¹² except that the entropy of methane is taken as 44.35, the value obtained spectroscopically by Giauque, Blue and Overstreet.¹³ Calculation of the equilibrium constant from this equation gives $k_1 k_2 k_3 k_4 k_5 / r_1 r_2 r_3 r_4 r_5 = 1.06 \times 10^8 \text{ mm.}^2$ at 760°; hence, for the greatest hydrogen concentrations of Table V, the correction for the re-synthesis of acetylene drops out, amounting to only 1 part in 10³; hence, r_5 may be put equal to zero. This was to be expected, since the greatest hydrogen pressures for which the rate was measurable are still far from equilibrium; it could scarcely be taken for granted, however. The ratio $k_1 k_2 k_3 k_4 k_5 / r_1 r_2 r_3 r_4 r_5$ turned out to be the square of the usual equilibrium constant; if it had been the square root instead, the value of r_5 could not have been neglected.

When the concentration of hydrogen is small enough, the rate given by this mechanism is simply

$$-(d[\text{CH}_4]/dt) = 2k_1[\text{CH}_4]$$

This accounts for the first-order constants of the early stages. When the hydrogen concentration is large enough, the first term in the denominator will become far larger than any of the others, and the rate will be

$$-(d[\text{CH}_4]/dt) = 2k_1 k_2 k_3 k_4 k_5 [\text{CH}_4]^2 / r_1 r_2 r_3 r_4 [\text{H}_2]^3$$

The constancy of the values of K in Table V shows that this relatively simple equation is valid over a considerable range; when it fails at the beginning of the reaction, K' remains constant. The implication of the constancy of K' , if this could be accepted at its face value, would be that for the entire range of concentrations the terms in $[\text{H}_2]$ and $[\text{H}_2]^2$ in the denominator remain unimportant. Actually, the accuracy available is far from sufficient to prove this and the variation of K' values from one experiment to another is of a sort that could be at least partially accounted for by the omission of these terms. To obtain any reliable values for the various coefficients would require much improved accuracy of the experimental rates.

From K of Table V, which for the late stages of the reaction equals $2k_1 k_2 k_3 k_4 k_5 / r_1 r_2 r_3 r_4$, we see that $k_1 k_2 k_3 k_4 k_5 / r_1 r_2 r_3 r_4$ is 0.03 cm.² min.⁻¹ or 3 mm.² min.⁻¹ at 760°. From spectroscopic free energy equations which will be published shortly, we find

¹² Storch, *THIS JOURNAL*, **53**, 1266, 4469 (1931).

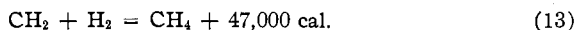
¹³ Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

$$K_p = \frac{[\text{H}_2]^3[\text{C}_2\text{H}_2]}{[\text{CH}_4]^2} = 0.11 \text{ mm.}^2 = k_1 k_2 k_3 k_4 / r_1 r_2 r_3 r_4$$

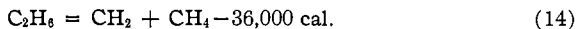
Together these results require $k_5 = 27 \text{ min.}^{-1}$ at 760° in a vessel with surface volume ratio of about 2 cm.^{-1} . The experiments presented here provide no evidence as to the homogeneity of the acetylene decomposition, but, judging by the work of Holliday and Gooderham, it is at least partially a wall reaction. The value for k_5 is in any case an approximate one, as it is based on a rather crude estimate for K_p . As nearly as can be told from work at atmospheric pressure, however, it is of the right order of magnitude. From the value of k_5 and the initial rate recorded in Table V, it may easily be computed that the partial pressure of acetylene in the beginning of the reaction was 0.07 mm. ; this appears to be a reasonable value.

The rate constants k_3 and r_3 are known at lower temperatures, the best measurements being those of Marek and McCluer¹⁴ and Pease;¹⁵ the extrapolated value of k_3 at 760° is 0.44 sec.^{-1} ; the partial pressure of ethane during the first part of Run No. C 1 was therefore about 0.007 mm.

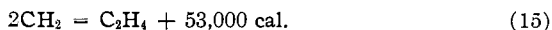
We can draw some conclusions also about the reactions involving CH_2 , though here we are on more uncertain ground. From the heat of reaction and activation energy of (3), the heat of activation for the reverse of (3)



is determined to be $32,000 \text{ cal.}$ The heat of activation of (5) is $73,000 \text{ cal.}$; that of



must be greater than $73,000 \text{ cal.}$, since the rate of this reaction must be less than that of (5). If we estimate $80,000 \text{ cal.}$, we can then calculate that the activation energy for (4) is $44,000 \text{ cal.}$ The rate constant for (4) will be approximately $10^{14} e^{-44000/RT}$ or, at 760° , $5 \times 10^4 \text{ cc. mole}^{-1} \text{ sec.}^{-1}$. In conjunction with the initial rate of Table V, this leads to a steady-state concentration of CH_2 , at the beginning of the reaction, of 0.07 mm. The bimolecular rate constant for



may be estimated as $10^{12} e^{-E/RT}$; the smaller value of the constant coefficient is reasonable in view of the simplicity of the molecule being formed. The value necessary for the energy of activation, to keep (15) from being more than a slight side reaction, is $24,000 \text{ cal.}$ This would mean an activation energy for (7) of at least $77,000 \text{ cal.}$; this seems to be an acceptable value.

In the experiments made by Storch with the lamp-bulb immersed in liquid nitrogen, the chief reaction products are ethane and hydrogen; any

¹⁴ Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931).

¹⁵ Pease, *THIS JOURNAL*, **54**, 1876 (1932).

hydrogen retardation which occurs is then directly assignable to the single reaction (13). It is unfortunate that due to experimental troubles which do not concern us the rate measurements under these conditions are extremely uncertain. It is clear, however, that at 1700° the rate constant for (13) is not greater than that for (4). Since the activation energy is 12,000 cal. less for (13), the associated constant factor must be but one-twentieth as large, or only 5×10^{12} cc. mole⁻¹ sec.⁻¹; since methane is about as simple a molecule as can be formed by a bimolecular association process, this smaller value is reasonable.

It appears, from the evidence available, that CH₂ is a comparatively inert substance, the activation heats for its addition reactions with methane, hydrogen and itself being 44,000 cal., 32,000 cal. and 24,000 cal. On the basis of these results an attempt will be made in this Laboratory to prepare the radical at lower temperatures and study it more fully.

For calculation of the maintenance of the rate of the unimolecular reaction (3) at low pressures, we have available experimental values for the vibrational frequencies. Dennison¹⁶ gave for the four different frequencies of the nine modes of vibration 4217 cm.⁻¹, 1520 cm.⁻¹ (double), 3014 cm.⁻¹ (triple) and 1304 cm.⁻¹ (triple). Villars¹⁷ has suggested that 2915 cm.⁻¹ in place of 4217 cm.⁻¹ will bring the assignment into agreement with Raman shifts without impairing the agreement with infra-red data. The change is in any case of little effect here, as the frequency remains so high as to be but rarely excited. At 1000°K. about 85% of the internal energy is due to the frequencies 1520 cm.⁻¹ and 1304 cm.⁻¹. Since it is not known how to use non-commensurable frequencies in calculating the behavior of unimolecular reactions, a natural procedure is to use a model of five oscillators all with the same frequency, which is so chosen that the energy content of the model at 1000°K. is equal to that of a methane molecule as calculated from the correct frequencies; when this is done, it is found that at 1 cm. pressure the rate should have fallen to perhaps a third of its high-pressure value. This result is not very satisfactory and the calculation was repeated with nine oscillators in the model, the total energy content being kept the same. The rate at 1 cm. pressure then came out 88% of the high-pressure value. It may therefore be concluded that there is probably no difficulty in accounting for the observed maintenance of the rate of this reaction.

It may be worth while to mention another procedure, in a way more rigorous, which might have been adopted for the calculations. By combination of the known frequencies it would be possible to determine the energies and quantum weights of all the activated states of methane. Reaction rates could be assigned to these levels in any way whatever, subject

¹⁶ Dennison, *Astrophys. J.*, **62**, 84 (1925).

¹⁷ Villars, paper presented at the New Orleans meeting, American Chemical Society, March, 1932; cf. Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

to the single easily applied condition that the correct activation energy was obtained. If no assignment could be found which satisfied this condition and gave satisfactory maintenance of the rate, it would be necessary to abandon the mechanism which has been suggested. It seems likely, however, that there would prove to be an ample margin of safety.

It is difficult to know what should be said about the induction period. The view that it represents the formation of steady state concentrations of the intermediate products became untenable when these concentrations were shown to be less than 0.1 mm. It can scarcely be caused by adsorption on the walls of the initial amounts of hydrogen produced, since in that case it would have become much more prominent in the packed vessel; actually, it was not observed at all. For a reaction of this character, it is almost unthinkable that any impurity could be responsible for an induction period. It would appear probable that the explanation lies in some peculiarity of the experimental arrangements, and that there is really no induction period at all.

Summary

The thermal decomposition of methane has been studied in quartz bulbs at 700–850°. The initial reaction is homogeneous and kinetically first order. The primary process is probably the unimolecular reaction $\text{CH}_4 = \text{CH}_2 + \text{H}_2$, with a rate constant $5 \times 10^{11} e^{-79385/RT}$; the observed rate constant is twice this, since the next step in the reaction is considered to be $\text{CH}_2 + \text{CH}_4 = \text{C}_2\text{H}_6$. The rate of methane decomposition is very greatly retarded by hydrogen; when this is present in sufficient quantity the reaction rate becomes proportional to $[\text{CH}_4]^2/[\text{H}_2]^3$. This result, together with the more complex hydrogen dependence of the intermediate stages, is fully accounted for by supposing that the ethane dehydrogenates in successive steps to ethylene, acetylene and finally carbon, and that all the reactions involved in the mechanism are reversible.

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NOTE

The Strength of Semicarbazide—and a Correction

BY NORRIS F. HALL

Bartlett¹ gives a value of 3.68 at 25° and $\mu = 0.079$ for the uncorrected acid dissociation constant (pK_A) of semicarbazide cation. This prompts me to call attention to the value of 3.65 for the same constant, obtained here² by Dr. Marshall R. Sprinkle by a similar method at 26° and at ionic strengths between 0.05 and 0.046. These two independent determinations seem to settle the question.

¹ Bartlett, *THIS JOURNAL*, **54**, 2857 (1932).

² Hall, *ibid.*, **52**, 5124 (1930).