[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Decomposition of Methane in an Electrical Discharge[1]

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RECEIVED JUNE 18, 1953

Decomposition of methane in a high-intensity electrical discharge yields acetylene and hydrogen, the only gaseous products in significant concentration, plus carbon. The 100 ev. yield (*i.e.*, *G* value) of acetylene calculated from previous work precludes a mechanism in which excitation of CH_4 molecule has a dominant role. Studies herein reported of the atmospheric pressure decomposition of methane, methane and hydrogen, methane and deuterium, and methane plus methane-d_4 suggest an explanation in which initial methane excitation furnishes only sufficient methyl radicals to start the process. The distribution of electron energies in the discharge appears to be non-Maxwellian and the C–H bond dissociation energy in free methyl less than that in methane. According to the mechanism suggested, CH_3 radical is the principal species excited and CH_2 produced therefrom is the free radical species present in important concentration. Phenomena interpreted on this basis are the production of CH_2D_2 in back reaction in presence of deuterium with only relatively insignificant yield of CHD_3 and CD_3H, the relatively great yield of HD from mixed methane and methane-d_4, and the calculated high *G* value (~31) of methane decomposition based on the work of Schoch. In the work here reported the maximum *G* found for such decomposition was 8.1 but the higher values are consistent both with this result and the mechanism suggested. The data presented include evidence for the elementary processes $CH_2 + H_2 \xrightarrow{M} CH_4$ and $CH_2 + CD_4 \rightarrow CH_2D_2 + CD_2$.

1. Introduction

Beginning with studies by Berthelot[3] in 1869 on the chemical effect of an electric discharge through methane, a variety of experiments has shown that acetylene is not only an important product of such reactions particularly at higher pressure, but also under optimum conditions of pressure, current density and flow rate, the only significant hydrocarbon product. Table I summarizes some typical examples of this work.[4–7] A more detailed discussion together with an attempt at explanatory mechanism has been given by Vasil'ev[8] but that paper does not, of course, include an examination of the implications of more recent work of Schoch.[7]

TABLE I

SUMMARY OF PREVIOUS RESULTS IN ELECTRIC DISCHARGE REACTIONS IN METHANE

Discharge	Pressure	*G*[a]	Principal hydrocarbon products	Workers
Spark	Atm.		C_2H_2	Berthelot[3]
Glow	2 mm.		~$5C_2H_6$:1 unsat.	Fischer and Peters[4]
	20 mm.		~$1C_2H_6$:2 unsat.	
			~$1C_2H_6$:16 unsat. with energy input doubled	
Glow cooled in liquid air	10 mm.	~ 2	~$1C_2H_6$:$1C_2H_2$	Yeddanapalli[5]
	10–50 mm.	~20	C_2H_2	Peters and Wagner[6]
			C_2H_4 decreases with increased pressure and energy input	
Glow in high-velocity gas stream	Atm.	~24 extrapolated	$0.75CH_4 \rightarrow C_2H_2$; remainder → mainly C	Schoch[7]

[a] $G = G(CH_4 \rightarrow {}^1/_2C_2H_2)$.

For the results at atmospheric pressure particularly, the reactions

$$CH_4 \longrightarrow 0.5C_2H_2 + 1.5H_2 \qquad (I)$$

$$CH_4 \longrightarrow C + 2H_2 \qquad (II)$$

sufficiently represent the over-all course. However, the low-pressure results indicate that the intermediate steps may involve free radicals. There is also the possibility (*cf.* Vasil'ev[8]) that free carbon may itself be an intermediate. Furthermore, products such as ethane and ethylene may result from side reactions not at all involved in the main process. However, any mechanism suggested in presumptive explanation of the chemical results must at the same time be in consonance with the high efficiencies reported for yield of acetylene per unit energy input.

Table I expresses yields in terms of number of molecules of methane converted to acetylene per 100 ev. input or, in the conventional nomenclature of radiation chemistry, as $G(CH_4 \rightarrow {}^1/_2C_2H_2)$. Reaction I requires 45 kcal. per mole of methane so that the maximum possible *G* value that can be attained cannot exceed 51.2. The maximum value shown by Schoch in the published literature is 24 for data extrapolated to infinitesimal conversion but this value is itself very large in view of the substantial additional contribution (~25% of the total decomposed) of reaction (II). Thus, the extrapolated value G(CH_4 decomposed) is ~31. Furthermore, one of us (M. B.) has been privately informed by Schoch that some unpublished data indicate even higher *G* values.

Definition of the temperature of a discharge is

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[1] Abstract from a thesis submitted by Hans Wiener in partial fulfillment of requirements for the degree of Doctor of Philosophy at the University of Notre Dame. Paper presented before Division of Physical and Inorganic Chemistry, meeting of American Chemical Society at Los Angeles, March 17, 1953.

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[3] M. Berthelot, *Ann. chim. phys.*, [4] **18**, 178 (1869).

[4] F. Fischer and K. Peters, *Z. physik. Chem.*, **A141**, 180 (1929).

[5] L. M. Yeddanapalli, *J. Chem. Phys.*, **10**, 249 (1942).

[6] K. Peters and O. H. Wagner, *Z. physik. Chem.*, **A153**, 161 (1931).

[7] E. P. Schoch, *et al.*, University of Texas Publication, No. 5011, "Acetylene from Hydrocarbons," June 1, 1950.

[8] S. S. Vasil'ev, *J. Phys. Chem. U.S.S.R.*, **20**, 517 (1946).

difficult. For discharges at 20 to 50 mm. thermocouples have registered temperatures of 400 to 1000°.[4] The Schoch process is accompanied by evolution of considerable heat. Whatever the significance of thermometric measurements and the nature of thermal energy distribution, the contribution of purely thermal effects cannot be ignored in view of the known production of acetylene from methane pyrolysis at atmospheric pressure and temperatures in the range 1000–2000°.[9] Thus, consideration of thermally activated steps is relevant to the explanation of the high G values of the electric discharge reaction.

Effect of flow rate (or the related fraction of methane converted) on $G(CH_4 \rightarrow {}^1/_2C_2H_2)$ indicates dependence of rate on methane concentration. The Vasil'ev 1946 analysis of the then available data indicated a first-order relationship.[10] However, when methane is initially diluted with hydrogen, the first-order "constants" increase with dilution. The Vasil'ev analysis shows decrease of the ratio of yields $G(C_2H_2)/G(\text{solid})$ with residence time in the discharge; the suggestion is that carbon and polymer result from secondary reactions of acetylene. In the Schoch process, the $G(C_2H_2/G(C)$ ratio appears constant.[7]

No attempt at detailed mechanism of the reaction has been published.

2. Experimental

2.1. **Survey.**—High rate of reaction in the glow discharge creates experimental difficulties for avoidance of which flow rate must be high and related to rate of energy input. Deposition of carbon on the electrodes introduces difficulties. In a limited current–voltage range, however, with suitable flow rates, experiments can be completed before carbon build-up becomes troublesome. Small flow rates permit use of a closed system convenient for study of mixtures, especially those containing gases (*e.g.*, methane-d_4) not available in large quantities.

2.2. **Apparatus.**—The electrode assembly was inserted into the flow system so that gas entered around the cathode and flowed out through the anode. The brass disc anode had flanges which were cemented to the glass tubing on each side; a central hole, 2 mm. in diameter, allowed passage of the gas through the anode. The cathode was a hollow copper cylinder through which water was circulated to prevent overheating. Its lower end was cone-shaped and the rounded apex of the cone projected into the hole in the anode. Consequent constriction of the gas flow in that region ensured passage of a maximum fraction of the gas through the discharge. A rubber collar, by which the cylindrical part of the cathode was held in the glass tube above the anode, allowed a slight side-ways deflection so that the electrodes could be touched together to strike the discharge. Vertical adjustment of the cathode permitted variation of the interelectrode distance.

The flow system consisted essentially of two gas burets, gas at atmospheric pressure being transferred from one to the other through the discharge by simultaneous movement of mercury reservoirs. These were suspended from the ends of a cable passing over pulleys above the burets so that, as one reservoir was lowered, the other was raised at the same rate. A second cable, attached to one of the reservoirs, was wound onto a motor-driven drum, and the flow rate could thus be controlled by adjustment of the motor speed. Springs served to counterbalance the considerable increase in weight as the reservoirs were lowered, and guide cables steadied their motion.

Gas could be admitted to the system by way of a stopcock next to the electrode assembly. The same stopcock served to separate reacted and unreacted gas at the completion of a run. A connection was also provided to the vacuum manifold. A sample tube attached thereto by means of a standard-taper joint could be removed for analysis of the product gases. Usual amounts of gas transferred during a run were 15–25 cc.

Direct current was supplied by a Westinghouse RA-60-A (Signal Corps) rectifier unit. The variable output voltage of the unit was usually adjusted to 2000 v., *i.e.*, considerably above the discharge voltage so that the discharge current could be controlled by insertion of suitable dropping resistors. The circuit included a voltmeter and a milliammeter, and a relay as circuit breaker. This relay had a common circuit with the motor of the flow system and with an electric timer, so that discharge, motor and timer could be switched off simultaneously.

2.3. **Materials.**—The gases used were methane, ethane, ethylene, hydrogen, deuterium and deuteromethane. With the exception of the last of these, all were obtained commercially (deuterium from Stuart Oxygen Co. by permission of the Atomic Energy Commission, the other gases from The Matheson Co., Inc.) about 99% pure, and were used without further treatment. Mass-spectrometric analysis gave the following composition for the methane: CH_4, 99%; C_2H_6, 0.6%; C_3H_8, 0.2%; N_2, 0.2%.

Methane-d_4 was prepared by two different methods. The first sample obtained by action of heavy water on aluminum carbide had the composition: CD_4, 79.3%; CD_3H, 13.2%; CD_2H_2, 7.5%. A second methane-d_4 sample prepared by reduction of carbon dioxide with deuterium over a nickel catalyst[11] had the composition: CD_4, 95.2%; CD_3H, 3.4%; CO, 1.4%.

2.4. **Analysis.**—All gas analyses were carried out with a Consolidated mass spectrometer No. 21-102, at the Sinclair Refining Co. Research Laboratories, Harvey, Illinois. The instrument could be relied upon to give gas compositions accurately to one part per thousand, except in the case of the rather complicated mixtures containing deuterated hydrocarbons, for most of which calibration samples were not available.

2.5. **Kinetic Measurements.**—The reciprocal of the flow rate of gas through the discharge was a measure of residence time. Analysis of gas and determination of yields of products thus gave information on relative rates of reaction. Variation of current (which could be approximately fixed by adjustment of external resistance and supply voltage) in four different ranges provided another variable which could affect rate. The discharge voltage, however, was not an independent variable. It was mainly a function of the interelectrode distance which, being only ~ 1 mm., could not be precisely adjusted. In consequence, the voltage was randomly varied within the arbitrary limits established by the apparatus itself.

3. Results

3.1. **Methane.**—Samples of pure methane were passed through the apparatus under conditions such as described in the previous section.

A typical product analysis follows:

	%		%
H_2	41.1	C_3H_8	0.1
CH_4	47.1	C_3H_4	0.1
C_2H_2	10.0	C_3H_4	0.2
C_2H_4	0.3	C_4H_2	0.2
		Air	0.2
C_2H_6	0.3	N_2, CO	0.4

For calculation purposes, the gases in the right-hand column were always neglected, as was also the ethane, since it never exceeded the amount present as impurity in the methane. From the remaining four components, the fate of the original methane was calculated according to the stoichiometric equations

$$2CH_4 \longrightarrow C_2H_2 + 3H_2$$
$$2CH_4 \longrightarrow C_2H_4 + 2H_2$$
$$CH_4 \longrightarrow C + 2H_2$$

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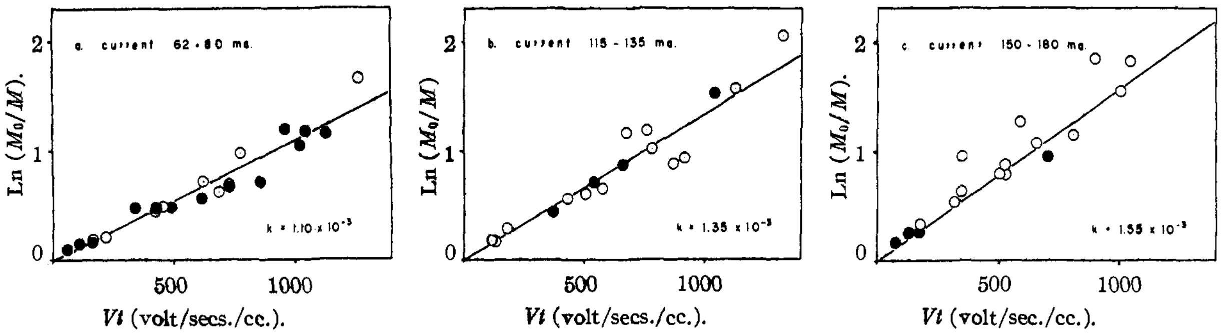
(9) F. Fischer, *Ber.*, **71A**, 56 (1938).

(10) Data reported for the Schoch process also fit the first-order law.

(11) K. Clusius and L. Popp, *Z. physik. Chem.*, **B46**, 63 (1940).



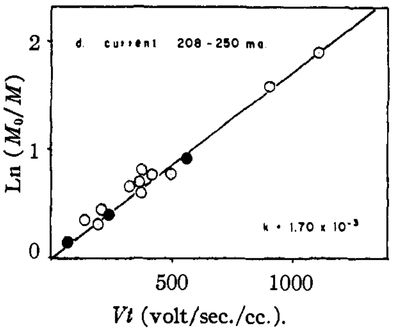


Fig. 1.—Effect of residence time and voltage on decomposition of methane. Dark circles represent runs in which actual analyses were made; *cf.* Table II.

In calculating the amount of methane left undecomposed, a correction was made for dead space, *i.e.*, connecting tubing that contained unreacted gas. The analysis was then expressed in terms of the fraction decomposed, D, and the fractions, α and ϵ, of the *decomposed* methane yielding, respectively, acetylene and ethylene. The current I, voltage V and reciprocal flow rate t, give the energy input per mole and enable calculation of the 100 ev. yield for methane decomposition. For the special case of gas at 25° and 760 mm. pressure, such calculation reduces to

$$G(\text{CH}_4 \text{ decomposed}) = 394\ D/IVt \qquad \text{(I)}$$

where I is in amperes, V in volts and t in sec. cm.$^{-3}$. The 100 ev. yield of acetylene production is given generally by

$$G(\text{C}_2\text{H}_2) = \alpha/2\ G(\text{CH}_4 \text{ decomposed}) \qquad \text{(II)}$$

Both initial and final gas volumes were measured. Comparison of the fractional increase with the theoretical value, given by $(1 - {}^1/_2\ \epsilon)D$, was therefore possible. The agreement was within about five per cent. with no systematic error. In view of the small value of ϵ, the fractional volume increase itself gave a good approximation for D. Consequently, analysis of the products of every run was unnecessary. Table II contains the data of runs for which analyses were made, and these runs are represented by the dark circles in Fig. 1. The light circles represent runs for which D was obtained from the volume change. These runs are not tabulated.

TABLE II

KINETIC DATA FOR METHANE[a]

Run[b] no.	Current, ma.	Volts	Time, sec.	D	α	ϵ	G[c]
	74	285	0.36	0.146	0.64	0.05	7.6
	80	150	.39	.097	.59	.06	8.1
	70	280	.57	.150	.75	.05	5.6
D8	70	310	1.08	.382	.70	..	6.4
	62	380	1.28	.385	.71	0.02	5.0
D10	71	315	1.34	.383	.99	0.05	5.0
D9	72	280	2.18	.432	.72	..	3.9
	70	300	2.43	.494	.81	0.02	3.8
	65	350	2.46	.511	.77	.03	3.6
	69	310	3.11	.703	.80	.03	4.2
	68	320	3.26	.695	.80	.02	3.9
	69	320	3.53	.690	.82	.02	3.5
D11	72	285	3.59	.649	.96	.04	3.5
	120	300	1.23	0.354	0.69	0.03	3.2
D12	140	400	1.35	.510	.85	.05	3.6
	122	360	1.84	.581	.77	.03	2.8
	118	340	3.07	.785	.79	.02	2.5
	180	190	0.38	0.152	0.54	0.02	4.6
	165	220	0.60	.224	.63	.02	4.0
	180	150	1.14	.226	.64	.01	2.9
	155	320	2.21	.618	.77	.02	2.2
	220	200	0.35	0.146	0.64	0.02	3.8
	208	195	1.23	.326	.68	.04	2.6
	212	240	2.34	.598	.71	.02	2.0

[a] Symbols explained in text. [b] Runs indicated by D numbers were made with methane–deuteromethane mixtures; numbers refer to Table IV. [c] Here G signifies $G(\text{CH}_4$ decomposed).

The method of plotting employed in Fig. 1 followed from some simple considerations of rate factors. The yield equation is of the form

$$f(M) = k' \times f(I) \times f(V) \times t \qquad \text{(III)}$$

where M is the final methane concentration, k' a constant. For each range of current it was found that a plot of D *vs.* Vt was smooth, *i.e.*, points did not deviate from the curves systematically with V. Thus, $f(V) = V$ was a satisfactory assumption. A straight line was obtained when $-\ln(M_0/M)$ (*i.e.*, $\ln(1 - D)$) was chosen for $f(M)$. For a given current, the data thus satisfied the first-order equation

$$-\text{d}M/\text{d}t = kVM \qquad \text{(IV)}$$

The constants of Fig. 2 conform to the relationship

$$k = \kappa I^{0.4} \qquad \text{(V)}$$

where κ is a constant. Thus, since k is approximately half-order in current, one interpretation is that approximately two radicals formed per primary physical process each result in disappearance of a methane molecule.

3.2. Methane–Hydrogen Mixtures.—The experiments on methane–hydrogen mixtures followed the procedure described for methane. The flow rate (hence t) was approximately constant for all runs, so that rate constants could not be obtained graphically. They were calculated on the assumption (*cf.* section 1) that the first-order relation for undiluted methane applied to that substance in the mixtures. The values thus obtained, together with the other data, are given in Table III.

TABLE III

KINETIC DATA FOR METHANE–HYDROGEN MIXTURES

Run[a] no.	CH_4, %	Current, ma.	Volts	Time, sec.	D	α	ϵ	G	10^3 k
	25	78	150	1.15	0.278	0.61	0.08	2.2	2.0
D1	25	72	230	1.01	.461	.69	..	2.7	2.7
	50	68	330	1.22	.642	.87	0.05	4.6	2.6
D3	50	70	300	1.16	.416	.82	..	3.4	1.6
D5	50	83	130	0.60	0.190	0.92	..	5.8	2.7
	60	68	270	1.29	.485	.75	0.04	4.8	1.9
	75	68	260	1.20	.328	.75	0.02	4.6	1.3
D6	75	72	270	1.25	.445	.79	..	5.4	1.7
(72 ma. average current: for undiluted methane $10^3k = 1.1$)									
	25	180	140	1.18	0.290	0.83	0.08	1.0	2.1
D2	25	172	200	1.06	.346	.79	..	0.9	2.0
	50	180	150	0.87	.246	.9	0.07	2.1	1.8
D4	50	176	200	1.07	.303	.96	..	1.6	1.7
	60	172	185	1.48	0.421	0.73	0.04	2.2	2.0
	75	150	170	0.88	.227	.75	0.04	2.9	1.7
D7	75	174	200	1.14	.303	.79	..	2.3	1.6
(172 ma. av. current: for undiluted methane $10^3k = 1.6$)									

[a] Numbers refer to Table IV. In runs labeled D, deuterium was used instead of hydrogen.

The rate "constants" appear to increase with dilution of the methane. The increase may not be significant in view of the reduced reliability of analyses of samples with low hydrocarbon content; but, since a similar effect was reported by Vasil'ev,[8] it cannot be discounted. The increase would signify that the rate of methane decomposition is not only a function of the methane concentration, but also of the nature of the diluent, the "effective concentration" of methane being higher in a mixture containing mainly hydrogen than in one containing the decomposition products in their usual proportions. The values of α and ϵ are also rather larger, particularly in the high current range, than those obtained with undiluted methane; *i.e.*, rather less carbon is formed in presence of excess hydrogen.

3.3. **Methane–Deuterium Mixtures.**—Data on a number of runs in mixtures of methane and deuterium in various proportions are included with those for hydrogen in Table III. Table IV shows the detailed analysis of the products.

The methane columns in Table IV provide an indication of the importance of back reactions. Between 10 and 25% of the methane decomposed goes to the formation of deuterated methanes; undoubtedly also some of the apparently undecomposed methane has been re-formed in back reactions. Among the deuteromethanes produced, CH_2D_2 is by far the most abundant.

The acetylene columns indicate the considerable extent to which isotope exchange occurs with this product or with intermediates involved in its formation. In a mixture of equal parts of methane and deuterium, there are two hydrogen atoms to one of deuterium; yet the acetylene formed from such mixtures contained the isotopes in roughly equal amounts.

The hydrogen–deuterium exchange can be estimated quantitatively from the H_2:HD:D_2 ratios. In a completely equilibrated mixture containing h atoms of hydrogen and d of deuterium this ratio would be $\sim h^2:2hd:d^2$; in the present case the exchange was evidently not complete. Careful interpretation of the data to give information on exchange would require consideration of the amount of deuterium entered into hydrocarbons. However, the fraction of deuterium exchanged is roughly indicated by comparison of HD produced and D_2 initially present. Table V shows such a comparison and also reveals that the fraction of deuterium exchange increases relative to the fraction of methane decomposed both with *decreasing* deuterium concentration and with increasing current. The explanation of this result may be found in an increased probability of the exchange H + D_2 → HD + D with increased temperature (corresponding to increased current) and an increased importance of this contribution when the deuterium concentration is relatively low.

TABLE IV

ANALYTICAL DATA FOR METHANE–DEUTERIUM MIXTURES[a]

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	H_2	HD	D_2	C_2H_2	C_2HD	C_2D_2
Initial mixture	*100*							*300*			
Run no. D 1	37.5	2.0	10.5	2.6	1.3	43.4	134.1	197.8	0.7	7.9	7.2
D 2	51.6	[b]	11.3	1.9	0.6	32.7	106.9	215.7	0.6	6.3	6.3
Initial mixture	*100*							*100*			
Run no. D 3	50.5	[b]	7.5	0.4	...	51.6	55.2	59.2	6.7	9.1	1.2
D 4	63.7	0.7	4.6	.7	...	33.7	50.2	62.4	3.3	7.3	4.0
D 5	77.9	...	2.8	.3	...	21.3	26.6	81.3	2.2	4.4	2.2
Initial mixture	*100*							*33.3*			
Run no. D 6	50.4	1.0	4.1	[b]	...	63.1	25.8	16.2	11.1	5.1	1.3
D 7	60.3	[b]	9.4	[b]	[b]	42.9	22.6	16.7	6.4	4.0	1.6

[a] The values are given in "per cent. relative to original methane." [b] Trace.

TABLE V

DEUTERIUM EXCHANGED WITH HYDROGEN AS A FUNCTION OF INITIAL DEUTERIUM FRACTION, CURRENT AND FRACTION OF METHANE DECOMPOSED

Run no.	Initial D_2 fraction	Current, ma.	Ratio, R, HD/D_2 (init.)	D	R/D
D1	0.75	~ 72	0.445	0.461	0.964
D3	.50		.552	.416	1.35
D5	.50		.266	.190	1.40
D6	.25		.774	.445	1.74
D2	0.75	~172	0.356	0.346	1.03
D4	.50		.502	.303	1.66
D7	.25		.678	.303	2.24

TABLE VI

ANALYTICAL DATA FOR METHANE–DEUTEROMETHANE MIXTURES

The values given are in "per cent. relative to original total methane."

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	H_2	HD	D_2	C_2H_2	C_2HD	C_2D_2
Initial mixture[a]	*51.3*		*3.4*	*6.0*	*36.0*						
Run no. D 8	30.3	...	4.8	4.2	21.3	21.7	29.7	10.3	3.9	7.0	2.2
D 9	29.1	...	2.6	3.9	19.9	23.0	33.3	11.6	4.3	7.9	3.2
Initial mixture[a]	*48.9*			*1.7*	*48.2*						
Run no. D 10	24.8	...	8.1	1.5	26.3	16.2	27.1	13.9	4.3	8.5	4.6
D 11	14.1	0.9	3.4	1.6	13.9	24.4	48.3	23.7	8.1	15.2	7.8
D 12	20.8	...	5.9	1.6	21.6	20.2	38.6	19.4	5.5	10.6	5.5

[a] Traces of air, CO and higher hydrocarbons were initially present.

3.4. Methane–Methane-d_4 Mixtures.—Table VI gives the analyses of runs made with mixtures of methane and methane-d_4. With due consideration given to the presence of CD_3H in the initial mixture, the methane columns again show preferential formation of CH_2D_2 with no production of CD_3H or CH_3D at moderate CH_4 conversion. The acetylene columns show, approximately, the expected statistical distribution of the isotopes.

The $H_2:HD:D_2$ ratio is again subject to quantitative treatment on the basis of the ratio $h^2:2hd:d^2$. Thus, in run D8 the approximate statistical amount of HD is 29.9 compared with the observed value 29.7. In the five runs summarized in Table VI, divergences between observed and calculated HD values are 1, 2, −10, 0 and −3%, respectively. These discrepancies do not appear significant. The result indicates that no large proportion of the hydrogen and deuterium is initially formed as molecules split off from one carbon atom, and the important decomposition reactions must therefore be those of the type

$$CH_4 \longrightarrow CH_3 + H;\ CH_3 \longrightarrow CH_2 + H;\ \text{etc.}$$

It is noteworthy that this conclusion is required in spite of the preponderance of CH_2D_2 among mixed methanes when deuterium is present either as initially added deuterium or initially added methane-d_4.

The inference from these results is that CH_2 radicals are probably present in the discharge in concentration relatively high compared to other radicals, and that they are probably formed stepwise.

3.5. Methane–Ethane and Methane–Ethylene Mixtures.—Runs in mixtures of methane with ethane and ethylene indicated that neither of those substances could be intermediates in the formation of acetylene. No ethane and very little ethylene is found in the product from pure methane. Consequently, each of these compounds, if formed, would have had to decompose almost completely during its time of residence in the discharge, and would thus have had to decompose relatively more rapidly than methane, which does not decompose completely under the conditions used.

The results obtained with the mixtures follow.

	Ratio CH_4/C_2H_6		Ratio CH_4/C_2H_4
Initial mixture	3.00	Initial mixture	2.56
Product	3.02	Product	2.46

There is thus no appreciable difference in the relative rates of decomposition of methane, ethane and ethylene, so that the last two of these are probably not intermediates in acetylene formation.

3.6. Characteristics of the Discharge.—A detailed study of the physical characteristics of the discharge was impracticable both because of its small dimensions and because of rapid carbon build-up. In the lowest range of current (60–80 ma.) the discharge was confined to one sector of the annular electrode gap and deposited spots of carbon on the electrodes. In the highest range (~200 ma.) the gap appeared to be filled by the discharge and carbon was usually deposited symmetrically. In appearance the discharge resembled a carbon arc, glowing brightly with a yellowish color especially at high currents. This glow appeared to be connected with the presence of carbon particles, for it was discontinuous and diminished with decreasing current. At the lowest currents a steady blue glow became apparent; this seemed to be the "natural" color of the discharge.

The volume of the discharge clearly varied with the power input, and was estimated at 1–10 mm.^{3} A reciprocal flow rate (t) of 1 sec. cm.$^{-3}$ thus corresponded to a residence time of 1–10 millisec.

Difficulties resultant from carbon build-up prevented direct study of the character of the discharge in methane. However, some experiments with hydrogen and with air served qualitatively to confirm the following picture of the discharge. Essentially, it is similar to the commonly described glow discharge at lower pressure. The high pressure of this work (*i.e.*, atmospheric) reduced the discharge length and made for high local temperatures which caused local turbulence and wiped out the sharp boundaries between discharge regions, *e.g.*, negative dark space, negative glow, etc. An indication of the high temperatures that can be reached locally was provided by the fact that an air discharge under similar conditions would melt Pyrex glass.

The discharge in methane could not be studied for larger electrode distances than about 3 mm. because of almost immediate carbon-filament formation across the gap. A discharge chamber with rotating electrodes and brushes for removal of carbon failed to overcome this difficulty; even with such an arrangement, a carbon path for the current would be formed quickly, and quantitative results were not obtained. Qualitatively, the methane discharge resembled that in air or hydrogen showing a lateral spreading of the positive column with increasing electrode distance.

4. Discussion

4.1. Efficiency.—The present laboratory-scale experiments did not reproduce the efficiency of the plant-scale process[7]; the products are however the same for the same fraction decomposed. Moreover, the first-order kinetics conform to the Vasil'ev[8] analysis of data obtained at lower pressures. Thus, the over-all chemical process in the discharge reaction appears fairly constant, except in regard to efficiency, over a considerable range of pressure and the general mechanism probably remains the same throughout. Consequently, any mechanism suggested for the results reported must be consistent with the highest efficiency elsewhere reported. A corollary of this conclusion is that relatively low efficiencies in the present case must be attributable to effects or circumstances relatively unimportant in the high efficiency reactions.

Effects which may have a bearing on the energy efficiency of the reaction are perhaps to be sought in the character of the discharge itself or, as is mentioned in section 4.4, in its intensity. Characteristic regions of the discharge include dark spaces, negative glow, and positive column. Only the latter increases with electrode separation and corresponding voltage increase. Increase of pressure, with corresponding voltage increase, has relatively the same effect, for in this case the relative length of discharge occupied by the positive column increases. However, Yeddanapalli[5] reports that the energy efficiency of decomposition is greater in the negative column than in the positive column; *i.e.*, per unit voltage drop more decomposition occurs in the negative glow than in the positive column. Thus it is improbable that increased voltage, characteristic of high pressure reactions, is of itself adequate to account for the high yields reported by Schoch[7] and by Peters and Wagner.[6]

An alternative explanation of their results may be sought in the fact that Schoch and also Peters and Wagner have used high velocity of gas flow to spread out the discharge in such a way that the interelectrode distance is effectively increased during a single pulse of the discharge. The discharge character under such conditions does not correspond to the steady state ultimately attained in relatively quiescent gas. It is beyond the intention of this paper to speculate unduly about effects which have not been measured. However, theory[12] indicates that the volume of the negative glow in the stationary state is determined by space charge set up by positive ions. The effect of a high-velocity wind on space charge and on average volume of negative glow may prove an important consideration.

4.2. Thermal Reaction.—The evidence indicates possible high temperature in the atmospheric pressure discharge. Consequently, it is necessary to consider the maximum possible contribution of thermal dissociations to the over-all reaction. If the temperature be sufficiently high for methane to decompose thermally at the rates observed, we can postulate the extreme condition that the function of the discharge is solely to maintain this temperature.[13] The efficiency would then be determined by the relative rates of reaction and of cooling, and would not be inherent in the chemical mechanism. If, as it will appear, thermal dissociations are not rate-determining, high temperature may still be an important factor in promoting the efficiency of the reaction, enabling it to proceed by steps that require appreciable activation energy.

The maximum temperature attainable can be calculated from the rate of energy input. On the hypothesis that high temperature is responsible for reported high G values, this temperature cannot exceed that calculated for the condition of maximum $G(\mathrm{CH_4}$ decomposed$) \sim 31$ in the reported work of Schoch.[14] The energy input of ~ 74 kcal. per mole decomposed in that case is ~ 29 kcal. greater than ΔH for reaction I. Assuming that the excess energy does not go into products and that it is not generally dissipated but is instead concentrated in 3 new molecules of methane for every 2 of them decomposed, it can be shown from heat capacity data[15] that the final temperature (if such a term can be properly applied) of the thermally excited methane molecules passing through the discharge does not exceed 1100°K.

Since the residence time of gas in the discharge is of the order of 10^{-3} seconds, a molecule or radical makes only about 10^7–10^8 collisions while in the discharge. At 1100°K., $\exp(-E/RT)$ is about 10^{-8} if E is ~ 40 kcal. Allowing for the fact that the temperature is the maximum attainable under the assumed conditions for which it was calculated, it is probably safe to suppose that reactions with activation energies greater than 40 kcal. cannot occur during the time of residence of the gas. This result excludes the thermal dissociation of methane or any of the $\mathrm{C_1}$ radicals, and hence the possibility that the formation of acetylene is entirely a thermal process.

4.3. Energy Transfer in the Discharge.—Since some of the principal steps in the mechanism are not thermal, but are due to electron impact processes, it becomes necessary to inquire how such processes can lead to the high efficiencies observed. It has already been shown that in some circumstances only 3.2 ev. of energy are consumed per molecule of methane decomposed. The absorption spectrum of methane begins at about 1870 Å.,[16] equivalent to 6.6 ev. which presumably represents the energy of the lowest optically attainable excited state. One excitation of a methane molecule would thus have to yield decomposition of two molecules, with formation of acetylene. Though there may be a mechanism whereby such a process can occur, it seems unlikely that it would be correct, since no margin at all is left for energy waste. In any event, the electron impact processes must be very largely of the most efficient kind; that is, they must lead to excitation of the lowest repulsive or weakly attractive states, and the amount of energy transferred in "doses" insufficient to cause dissociation, *e.g.*, in elastic collisions, must be small.

Actually, low-voltage electron excitations lead to low-lying states access to which may be forbidden in a light absorption process. Thus, such ex-

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(12) *Cf.* K. K. Darrow, "Electrical Phenomena in Gases," William and Wilkins, Baltimore, Md., 1932.

(13) The mechanism for a purely thermal process is that the electrons transfer a significant fraction of their energy to molecules in inelastic collisions on each impact. The fraction transferred depends on the energy of the electron and the molecule struck; *e.g.*, for an electron swarm of mean energy 0.2 ev. the inelastic loss is 5.8 times the elastic loss for $\mathrm{H_2}$, 2000 times for HCl, 6000 times for $\mathrm{N_2O}$, 650 times for $\mathrm{NH_3}$ (calculated from H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, p. 279). As one extreme, we conceive the situation that no electrons attain energy sufficient to excite but that all the energy is lost in low-value energy transfers occurrent in inelastic collision at low energy. At the other extreme, we may imagine that no energy is so lost and all electrons attain energy sufficient to cause electronic excitations and that such transfers are alone responsible for the effects observed. Actually, the effect of low-energy inelastic collisions is to decrease both the electron temperature and the amount of energy made available for chemical processes *via* electronic excitation.

(14) In this calculation the assumption is that acetylene is first produced and that carbon results from its decomposition.

(15) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

(16) H. Sponer, "Molekülspektren I," Julius Springer, Berlin, 1935.

citation of a stable molecule (singlet) usually leads to a low-lying (triplet) state the lower range of which may be stable.[17] The lowest energy of the triplet state of significance for glow-discharge reactions is therefore the minimum necessary for a decomposition; *e.g.*, E_M, the bond-dissociation energy of the C–H bond = 4.4 ev. in the case of methane.[18] The minimum energy necessary for dissociation of a CH_3 radical (excited presumably in an optically forbidden transition to a quadruplet state), E_m, is not so well established. Dependent on the value accepted for the heat of sublimation of graphite arguments may be adduced for a value of E_m anywhere in the range 3.7–4.8 ev. At most the energy difference, $E_M - E_m$, between the lowest chemically significant states (*i.e.*, states which can decompose) is 1 ev. For calculation of the relative *a priori* probabilities of excitation of those two states under conditions of the discharge the electron energy distribution must be known.

In calculation of electron energy distribution, rate of energy gain from the field is equated to rate of energy loss to the gas molecules. In a simple treatment, E_{av}, the average energy of the electrons, is given[19] by

$$E_{av} = eX\lambda/2\alpha^{1/2} \qquad \text{(VI)}$$

where e is the charge on the electron, X the field strength, λ the mean free path, and α the fractional energy loss per collision. If it is supposed that an electron collides with every molecule whose center is within one collision radius of its path, and if 1.6 Å. is taken for the collision radius of methane,[20] the mean free path of an electron[21a] is $\ngtr 2 \times 10^{-4}$ cm. at 760 mm. even at 1000°. With the field strength in the methane discharge about 10^3 volt cm.$^{-1}$, equation VI yields $E_{av} = 0.1\alpha^{-1/2}$. In the extreme α has the elastic collision value. However, in the cases reported[13] inelastic scattering appears very important and α has been generally stated to have several hundred times the elastic collision value. A lower limit is $\alpha \nless 0.01$. Thus, $E_{av} \ngtr 1$ ev. On the other hand, if we adopt the more reasonable value $\alpha = 0.04$, E_{av} has the correspondingly smaller value, 0.5 ev.

On the basis of the value $E_{av} \sim 0.5$ ev. it follows from the Maxwell distribution that the lowest significant excitation is exp (1/0.5) $\simeq$ 7.4 times as probable for a free methyl radical as for a methane molecule (*i.e.*, $\rho = 7.4$), if the two are present in equal concentration and if $E_M - E_m = 1$ ev.

The foregoing calculation involves the implicit assumption of Maxwellian energy distribution of the electrons.[21b] According to Loeb the assumption of nearly Maxwellian distribution is justifiable for the electron densities characteristic of an essentially quiescent positive column. However, it appears from section 4.4 that a much higher value of ρ is required and it is thus desirable to inquire whether assumption of another energy distribution (under the turbulent conditions of the type of discharge used in this work) would yield more satisfactory values. We consider two other energy distribution functions: that of Townsend[22]

$$W(E) = \frac{N}{E_{av}\sqrt{\pi}} \exp\left[-\left(\frac{E}{E_{av}} - 0.85\right)^2\right] \qquad \text{(VII)}$$

and that of Morse[23]

$$W(E) = \text{const}\,\frac{E^{1/2}}{E_{av}{}^{3/2}} \exp\ [-0.847(E/E_{av})^2] \qquad \text{(VIII)}$$

and calculate the comparative results shown below.

$E_M - E_m$, ev.	1		0.3	
E_{av}, ev.	1.0	0.5	1.0	0.5
(Maxwell)	2.7	7.4	1.3	1.8
(Townsend)	$10^{14.6}$	10^{64}	$10^{4.6}$	$10^{20.7}$
(Morse)	$10^{15.3}$	10^{61}	$10^{4.8}$	$10^{19.5}$

We have seen from section 3.4 that the concentration of free CH_3 in the discharge is maintained very low, even in comparison with free CH_2. Since the activation energy for thermal decomposition of CH_3 to yield CH_2 is certainly ~4 ev., that reaction does not occur preferentially in the discharge. The only alternative conclusion is that discharge-induced decomposition of free methyl does occur preferentially. The table in the preceding paragraph shows that such a reaction can occur preferentially even in the presence of large excess of methane provided that the energy distribution of electrons has a non-Maxwellian form with depletion of the higher energy range. Such departure may be expected most notably at electron energy levels near the excitation levels of the molecular system they traverse.

Preferential excitation of low-energy states also accounts for the behavior of methane–hydrogen mixtures. The lowest excitation potential of hydrogen is ~11 ev.,[23a] which is so far above the lowest excitation level of methane, that very little excitation of hydrogen can occur, and dilution by hydrogen does not greatly affect the dissociation of methane and its fragments. Dilution by the products, on the other hand, introduces a species with a presumably very low excitation potential to a low-lying triplet state (*i.e.*, acetylene, <5.2 ev.[16]); hence the rate is reduced as the methane decomposes. Similarly, the occurrence of relatively little exchange in mixtures of methane and deuterium can be attributed to the infrequency of primary deuterium dissociation.

4.4. Mechanism.—Any mechanism offered in explanation of the results must conform to the following special requirements: (a) The energies involved must permit a yield $G(CH_4 \rightarrow {}^1/_2\ C_2H_2) \sim 24$ when extrapolated to the condition of negligible methane conversion (*cf.* sections 1 and 4.1).

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(17) *Cf.* consideration of the water molecule by K. Niira, *J. Phys. Soc.. Japan*, **7**, 193 (1952); also. G. G. Hall. *Proc. Roy. Soc.* (*London*), **A213**, 113 (1952); R. G. Parr, D. P. Craig and I. G. Ross, *J. Chem. Phys..* **18**, 1561 (1950).

(18) *Cf.* M. Szwarc. *Chem. Revs..* **47**, 75 (1950).

(19) This is the familiar equation given by Darrow (ref. 12, p. 177) except that the more general term α is introduced for the fractional energy loss on collision. The simple treatment employs an elastic collision model and sets $\alpha = 2m/M$. where m and M are the electron and molecule masses. respectively.

(20) E. Mack, Jr.. THIS JOURNAL. **47**, 2468 (1925).

(21) (a) In such calculation, the assumption is made of no specific molecular interaction dependent on electron velocity. Such assumption is well-known not to be justifiable: λ varies as a function of energy in a way characteristic of the gas. *Cf.* L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases." John Wiley and Sons, Inc., New York. N. Y.. 1939, pp. 180, *et seq.* (b) *Ibid..* p. 585.

(22) J. S. Townsend. *Phil. Mag..* **9**. 1158 (1930); *cf.* ref. 21. p. 210.

(23) *Cf.* F. Block and N. E. Bradbury. *Phys. Rev.*, **48**. 689 (1935).

(23a) G. Glockler. *J. Phys. Chem..* **52**. 451 (1948).

(b) Free radicals intermediate in acetylene production must be produced stepwise from methane decomposition (*cf.* section 3.4). (c) Decomposition reactions involving elimination of a molecule of hydrogen from a single methane parent must be unimportant contributors to the total effect (*cf.* section 3.4). (d) The concentration of CH_3 must be low relative to that of CH_2 (*cf.* section 3.4). (e) The mechanism must permit a kinetic scheme in which the average rate of methane disappearance is approximately first-order in methane and half-order in current (*cf.* sections 1 and 3.1). (f) Compounds such as C_2H_6 and C_2H_4 cannot be involved as intermediates (*cf.* section 3.5). (g) Activation energies of any of the steps cannot exceed ~40 kcal. (*cf.* section 4.2). Thus, chain initiation by "thermal decomposition" of methane is inadmissible.

A mechanism meeting these special, and the usual general, requirements follows.

The discharge-induced reaction

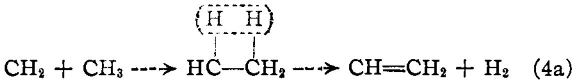
$$CH_4 \rightsquigarrow CH_4^* \longrightarrow CH_3 + H \qquad (1)$$

makes a negligible contribution to the total methane consumption (*cf.* section 4.3) but does provide the few radicals and atoms needed for the relatively more important subsequent processes

$$H + CH_4 \longrightarrow CH_3 + H_2 \qquad (2)$$

$$CH_3 \rightsquigarrow CH_3^* \longrightarrow CH_2 + H \qquad (3)$$

Reaction (3) occurs much more frequently than does reaction (1) (*cf.* section 4.3) and is the important process for electrical excitation of the gas. It has such high probability that the concentration of CH_3 relative to CH_2 remains low.[24] The latter can react with CH_4 to form two CH_3 radicals but to accommodate all the requirements listed above we have found it necessary instead to assume a relatively high probability for a rather unusual reaction



$$CH_2 + CH_3 \dashrightarrow \overset{(H\ \ H)}{HC{-}CH_2} \dashrightarrow CH{=}CH_2 + H_2 \qquad (4a)$$

$$CH{=}CH_2 \longrightarrow CH{\equiv}CH + H \qquad (4b)^{25}$$

Reaction (4) (*i.e.*, 4a plus 4b) must compete also with the chain-termination process

$$CH_2 + H_2 \xrightarrow{M} CH_4 \qquad (5)$$

Evidence for presence of CH_2 in this work is supported by the actual detection by Letort and Duval[26] (using a tellurium mirror technique) of important quantities of free CH_2 radical in the high-frequency discharge in methane. Both the predominance of CH_2D_2 in the products of discharge in a gaseous mixture containing D_2 (*cf.* section 3.4 and also Table IV and VI) and the evidence of Bawn and Milstead[27] on behavior of CH_2 and molecular H_2 in a Polanyi sodium-flame furnish support for reaction (5). However, it does not follow that reaction (5) is important in the ordinary decomposition of pure methane. Table IV shows that in a mixture containing really large quantities of deuterium, relatively small amounts of CH_2D_2 are produced even on substantial decomposition of CH_4. Furthermore, the facts that decomposition is approximately first order in methane and that the first-order constant actually increases in presence of hydrogen (section 3.2) indicate that reaction (5) makes a relatively unimportant contribution as compared with the enhanced probability of methane excitation in a hydrogen atmosphere (section 4.3).

An undoubtedly weak feature of the mechanism suggested is the necessity of a reaction like (4a). Superficially, it appears to violate the principle of minimum nuclear motion[28] but, as Rice and Teller[29] have indicated, that principle is generally to be applied only to reactions involving completely bonded carbon atoms. A "sticky" collision involving a splitting-out of H_2 from adjacent carbon atoms is not impossible. It is assumed here because its activation energy appears decently low, because it gives molecular hydrogen in which the atoms have been initially bonded to different carbons, and because it provides a free H atom which serves *via* reaction (2) to maintain an energy requirement that each excitation of a free CH_3 is associated with decomposition of two methane molecules.

Furthermore, while we are properly apologetic about the assumption of a reaction like (4), it is apparent from other work, *e.g.*, that of Muller and Peytral[30] and Knox, Norrish and Porter,[31] that the chemical reactions occurrent in a mixture containing a high concentration of free CH_2 are far from simple and that, at the very minimum, an involved sequence of reactions is necessary for an explanation of the products. While we hold no special brief for reaction (4) as written, some equivalent sequence of permissible activation energy (*cf.* section 4.2) is required.

Roughly speaking, one may imagine the excitation potential $E(CH_3)$ to be ~4.4 ev. Thus, the mechanism described is consistent with $G(CH_4 \rightarrow {}^1/_2\, C_2H_2) \geqslant 31$, as suggested by the work of Schoch.[7]

In an idealized treatment of the kinetics of discharge-induced reactions one might consider a unit "piece" of gas entering the energy-transfer region at time t_0 and leaving it at time t_1. Depending on the time required for the totality of chemical reactions as compared with $t_1 - t_0$, the kinetics could be treated by either steady-state or sector methods. The latter, at best, would require modification because, although we might write for the rate of the electrically initiated reaction (3)

$$r_3 = k_3(CH_3)$$

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[24] Excitation of CH_2, in a process corresponding to reaction (3), is relatively improbable. The ionization potential $I(CH_2) = 11.9 \pm 0.2$ ev. (A. Langer and J. A. Hipple, *Phys. Rev.*, **69**, 691 (1946)). According to J. A. Hipple and D. P. Stevenson, *ibid.*, **63**, 621 (1943), $I(CH_3) = 10.0$ ev. The excitation potentials are probably correspondingly related.

[25] Occurrence of significant quantities of C_2HD in discharge reaction in CH_4-D_2 mixtures (*cf.* Table IV) suggests that reaction (4b) may be rapidly reversed. When D_2 is present in high concentration, the reaction $H + D_2 \rightarrow HD + D$ may provide enough free D so that the processes $C_2H_2 + D \rightarrow C_2H_2D$; $C_2H_2D \rightarrow C_2HD + H$; $C_2HD + D \rightarrow C_2HD_2$; $C_2HD_2 \rightarrow C_2D_2 + H$ become relatively important.

[26] M. Letort and X. Duval, *Compt. rend.*, **219**, 542 (1944).

[27] C. E. H. Bawn and J. Milstead, *Trans. Faraday Soc.*, **35**, 889 (1939).

[28] E. Peytral, *Compt. rend.*, **197**, 831 (1924); *Bull. soc. chim.*, **29**, 44 (1921).

[29] F. O. Rice and E. Teller, *J. Chem. Phys.*, **7**, 199 (1939).

[30] J. A. Muller and E. Peytral, *Compt. rend.*, **196**, 279 (1933).

[31] K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

the parameter k_3 would itself be a function of (CH_3), (CH_4), the pressure of the gas and the detailed nature of the discharge. If we ignore such factors as the effect of turbulence, we can write for the average rates

$$\bar{r}_2 \sim 2\bar{r}_3$$

and

$$\bar{r}_3 \propto \bar{r}_1 \propto (CH_4)$$

If the average rate of methane disappearance, $\overline{d(CH_4)/dt}$, could be equated to $\bar{r}_2$, we might then reach the rather satisfactory conclusion that $\overline{d(CH_4)/dt}$ would be approximately first order in (CH_4). Actually, we note that $\overline{d(CH_4)/dt} = \bar{r}_2 - \bar{r}_5$ and that the last term is not small relative to $\bar{r}_2$ when the amount of hydrogen present is high (*cf.* section 3.3). Thus, from the viewpoint of kinetic requirements the best that can be said about the mechanism proposed is that it does not obviously violate the need that the average rate of methane decomposition be first order in methane. In section 4.3 it has been shown that increase in the "first-order constant" on dilution with hydrogen is consistent with the theory of the electrical discharge.

The mechanism given suggests that carbon and polymer formed result from secondary reactions on acetylene, a result consistent with the report of Vasil'ev[8] that relatively less acetylene is formed with increased residence time. If anything, our results show an opposite effect (*cf.* Table II) but it is possible that this result is attributable to still another secondary effect; *i.e.*, the effect of atomic hydrogen on carbon deposits, which have been formed rather plentifully in our work.

Yet one other pair of reactions must be assumed to explain the totality of the results observed, namely

$$CH_2 + CD_4 \longrightarrow CH_2D_2 + CD_2 \qquad (6a)$$

$$CD_2 + CH_4 \longrightarrow CH_2D_2 + CH_2 \qquad (6b)$$

These reactions do not involve any great rearrangement of atoms in the activated complex, which probably involves a rather sticky collision. They are required to explain the almost exclusive yield of CH_2D_2 among mixed methanes formed in the discharge-induced reaction between methane and methane-d_4 (*cf.* section 3.4).

The general absence of CH_3D and CD_3H, the predominance of CH_2D_2, and the preferential excitation of CH_3 in the discharge (*cf.* section 4.3) all are consistent with a C–H bond dissociation energy in free methyl substantially lower than that in methane.

This reaction scheme has neglected consideration of many other obvious radical reactions. However, the conclusion for all those examined was that they could not have contributed importantly to the reaction scheme.

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Decomposition of Nitrosyl Disulfonate Ion. III. Reaction with Nitrous Acid and its Relation to the Mechanism in Acid Solution[1]

BY JAMES C. M. LI AND D. M. RITTER

RECEIVED MAY 16, 1953

The spontaneous decomposition of nitrosyl disulfonate ion has been further studied by observations in 1 *M* sodium acetate buffer solutions with and without added nitrous acid. With sufficient nitrous acid the rates of color fading and nitrous oxide evolution were proportional to $(\Sigma HNO_2)^2((SO_3)_2NO^-)^0$; the nitrous acid was regenerated by the reaction, and extra nitrous acid was formed. The spontaneous decomposition (no added nitrous acid) in the high capacity, high ionic strength buffer solution proceeded throughout by the branching chain mechanism previously reported, but with a scarcely observable initiating step. A mechanism was deduced in which the formation of N_2O_3 from nitrous acid was the rate determining step with $k_{N_2O_3} = k_1 = (kT/h)\, e^{-20,070/RT}\, e^{16.28/R}$.

In previous work[2] nitrous acid was found to act as an important intermediate in the branching-chain decomposition of nitrosyl disulfonate ion as observed in mildly acidic buffer solutions. Part of the evidence was the *p*H dependence of the chain-branching constant which could be interpreted as being related to the concentration of molecular nitrous acid. The investigation reported here had the object of inquiring further into the action of nitrous acid. This was accomplished by observing the reaction of that substance with nitrosyl disulfonate ion within a *p*H range where the spontaneous decomposition was slow. The reaction was best observed in high capacity buffer solutions[3] and thus required a restudy of the spontaneous decomposition under those conditions in order to compare the kinetics. With these data available it became possible to account for the spontaneous decomposition in unbuffered solutions.

Experimental Part

The color disappearance of nitrosyl disulfonate ion during reaction was measured at 540 mμ with a Beckman DU spectrophotometer using a ground-stoppered cell of one centimeter thickness placed in a chamber built in the light path of the spectrophotometer. The chamber was filled with water to about the shoulder of the cells, and the water was circulated continuously from a thermostated bath. The temperature variation in the chamber was ±0.01° at room temperature and ±0.02° at 35° and 10°.

For the collection of N_2O gas where reaction velocities were determined by observing that substance, the apparatus was similar to that described by Schubert.[4] All-glass seals were used and the 10 ml. micro-buret, the temperature equalizer and the water-filled differential manometer were

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[1] Abstracted from a thesis by J. C. M. Li, submitted to the Graduate School of the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.

[2] J. H. Murib and D. M. Ritter, THIS JOURNAL, **74**, 3394 (1952).

[3] 1 *M* sodium acetate as compared with 0.045 *M* previously used.

[4] W. M. Schubert, THIS JOURNAL, **71**, 2639 (1949).