The Mercury Sensitized Reactions of Methane, Deuteromethanes and the Hydrogen Isotopes

Kiyoshi Morikawa, W. S. Benedict, and Hugh S. Taylor

Articles you may be interested in

The Mercury Sensitized Reactions of Methane, Deuteromethanes and the Hydrogen Isotopes

KIYOSHI MORIKAWA,[1] W. S. BENEDICT[2] AND HUGH S. TAYLOR

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

(Received January 2, 1937)

The interaction of methane and deuterium and of methane and methane-d_4 under the influence of excited mercury have been studied. The influence of temperature, reactant concentration, light intensity and mercury concentration on the yield of deuteromethanes has been measured. Below 200° the results indicate that the production of deuteromethanes is governed by the photosensitized formation of free methyl radicals. At higher temperatures chain reactions become important and high quantum efficiencies of interaction are observed. A simultaneous process of condensation of methane to yield higher saturated hydrocarbons has been shown to occur and its kinetics and quantum efficiency studied. The condensation occurs in presence of hydrogen and its isotope. A sequence of reactions has been postulated and approximate energies of activation suggested which permit a description of the observed phenomena over the whole range of temperatures, light intensity and concentrations studied.

A PRELIMINARY investigation of the mercury photosensitized reaction between deuterium and methane[3] showed that interaction with formation of deuteromethanes occurred in the range of temperatures from 40° upwards, the temperature coefficient of the reaction indicating an activation energy of the order of 5 kcal. Since the quenching efficiency of deuterium for the resonance radiation of mercury is equal to that of hydrogen[4] and is therefore large at room temperatures with respect to that of methane,[5] the preliminary results indicated that the interaction of deuterium atoms and methane should be an efficient process with a low activation energy of the order of magnitude cited. Geib and Steacie[6] and more recently Steacie and Phillips[7] have brought forward evidence which indicates that the activation energy of the reaction is about 11 kcal. In the earlier work of these authors, deuterium atoms from a Wood's discharge tube were used. In the later work, both atoms from the discharge tube and the mercury sensitized reaction were studied. Our own investigations with the latter reaction, which have continued uninterruptedly since our first communication, have revealed that the processes occurring are very complex and that an accurate determination of the activation energy of the reaction in question cannot thus be obtained since other processes are producing deuteromethanes and reactions leading to condensation products of the hydrocarbon occur. In the following pages we record in detail the results of these more comprehensive studies since they yield much information concerning the fundamental reactions of atomic hydrogen isotopes and hydrocarbon radicals.

EXPERIMENTAL DETAILS

Materials

Hydrogen was obtained by the electrolysis of potassium hydroxide solutions, and purified by passage over platinized asbestos at 250° and through a liquid-air trap. Deuterium was similarly prepared from a $KOD - D_2O$ solution, oxygen impurities being removed over a hot platinum wire, to avoid dilution with hydrogen by exchange reactions.

Methane was prepared by reduction of carbon monoxide with excess hydrogen on a nickel catalyst at 255°, the excess hydrogen being removed over copper-copper oxide at 300°; the carbon dioxide formed in a side reaction was removed by soda lime and the water vapor in a solid carbon dioxide-acetone mixture. Repeated fractionation of the residue at liquid-air temperatures yielded the final pure product.

Methane-d_4 was prepared in essentially the same manner. The catalyst employed was re-

---

[1] Visiting Research Fellow of the Central Laboratory, The South Manchuria Railway Co., Dairen, Japan.

[2] National Research Fellow in Chemistry, 1933–1935.

[3] Taylor, Morikawa and Benedict, J. Am. Chem. Soc. 57, 383 (1935).

[4] Evans, J. Chem. Phys. 2, 445 (1934).

[5] Bates, J. Am. Chem. Soc. 52, 3825 (1930); 54, 569 (1932).

[6] Geib and Steacie, Zeits. f. physik. Chemie B29, 215 (1935).

[7] Steacie and Phillips, J. Chem. Phys. 4, 461 (1936).

duced in deuterium from the purest D_2O available. The final product was 96–98 percent C–D.

Apparatus and experimental method

A static method was employed shown in diagrammatic outline in Fig. 1. The light source S was a Hanovia Sc. 2537 lamp with the discharge tubing coiled into a flat spiral which could be placed parallel to the plane face of the quartz reaction tube V. The light from the source was normally filtered through a 25 volume percent solution of acetic acid passing continuously through the quartz cell F, the solution being renewed about once every half-hour. This served to eliminate the short wave-length radiation below 2537A. In a few experiments a $Cl_2 - Br_2$ gas filter was used. The radiation was collected by the quartz lens L and concentrated in an approximately parallel beam on the reaction vessel V placed inside and to the rear of an electric furnace, the front end of which was closed with a plane parallel quartz plate, P. The quartz reaction vessel was cylindrical, 12.8 cm long and 4.6 cm diameter, the front plane polished face of which was 12.5 cm from the plate P in a furnace 30 cm long and 6.3 cm internal diameter whose temperature could be controlled to $\pm 3°$. The supply of mercury vapor to the reaction cell came from a side tube M in which the mercury could be maintained either at 0° with ice-water or at 56° by boiling acetone in the surrounding vessel B, the acetone being condensed in C and kept dry by the calcium-chloride tube in the position shown.

The gases could be introduced by the capillary leak T into the reaction vessel either saturated with mercury vapor at a controlled temperature or freed from traces of water vapor by immersing the trap shown in solid carbon dioxide-toluene mixture.

The main portion of the apparatus shown in the diagram with a reaction volume of 230 cc and total volume of 270 cc was connected through a stopcock to the manometer, to a gas burette which also served as a Töpler pump, to an analytical train (which consisted of a copper-copper oxide tube and a fractionation trap)[7a] to
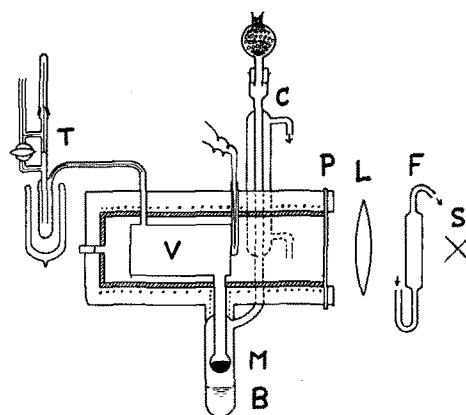

FIG. 1.

gas storage bulbs, to a McLeod gauge and to an evacuation train consisting of a mercury diffusion pump and an oil pump.

The cell could be cleaned between runs by applying an electric discharge to hydrogen in the cell at a pressure of several mm, the system being then thoroughly evacuated. The excellent reproducibility of experimental results testifies to the efficiency of this treatment after runs extending over a period of more than one year.

The light source was brought to constancy of operation by burning for at least one half-hour prior to use in an experiment. Mixtures of gases of known composition were then illuminated for a definite interval of time, the residual gases recovered by evacuation with a Töpler pump and introduced either into an analytical cell for analysis by infrared absorption or to the analytical train already described.

Analytical details

The progress of the exchange reaction between deuterium and methane and between methane and methane-d_4 was followed by measurement of the absorption at specific wave-lengths in the infrared region. This technique has already received detailed discussion.[8] The analysis was made in presence both of hydrogen and higher hydrocarbons produced during reaction, but measurements of absorption at the various wave-lengths due to one or other of the several substituted methanes served not only to give the percentage of C–D bonds in the mixture

---

[7a] K. Morikawa and N. R. Trenner, J. Am. Chem. Soc. **59** (1937).

[8] Benedict, Morikawa, Barnes and Taylor, J. Chem. Phys. **5**, 1 (1937).

but to identify and define the distribution of the deuteromethanes produced. In some cases the methanes were free from the higher hydrocarbons formed by fractional extraction at liquid-air temperatures and then analyzed. The results obtained by both methods were quite concordant.

The analytical data for the exchange reaction between methane and deuterium are expressed as percent $C-D$ in the product defined by the expression, $100(C-D)/(C-H+C-D)$. The quantum efficiency γ_e, equivalent in our experiments to quantum yield, is obtained from the expression $\gamma_e = 4 \times cc_{CH_4} \times$ percent $C-D/100tI_{abs}$ since CH_4 contains four $C-H$ bonds, and t is the time in hours, I_{abs} the intensity of resonance radiation $\lambda = 2537A$ absorbed expressed in cc per hour.

The reaction between methane and methane-d_4 is expressed as percentage attainment of equilibrium θ. In this case the quantum efficiency is given by $\gamma_e' = 0.5\theta \times cc_{(CH_4+CD_4)} \times 4/100tI_{abs}$. This assumes an equilibrium constant $K=1$, equilibrium corresponding to 50 percent $C-D$ in a CH_4+2D_2 mixture.

The condensation processes found to occur in these hydrocarbon systems were followed analytically by measuring the pressures at two constant volumes. The data in the succeeding tables refer to the pressures at a volume of 88 cc. The total gas recovered from a reaction was passed slowly through a liquid-air trap in which the higher hydrocarbons formed were solidified. The methane and hydrogen were extracted by a Töpler pump, the solid residue vaporized, recondensed and the extraction process repeated. The hydrogen-methane extraction was analyzed by passage over copper-copper oxide at 250–300°, the decrease in volume noted and the residual methane recovered through a solid carbon dioxide trap. We thus can measure the total pressure change, the amount of methane consumed $(-\Delta CH_4)$, the higher hydrocarbons produced $(+\Delta H - HC)$ and the hydrogen produced $(+\Delta H_2)$. The average formula of the higher hydrocarbons (C_nH_m) can be learned approximately by compressing the gases, after vaporization, to 10 cc volume and measuring the vapor pressure at $-80°$ and room temperature. The ratio of these two pressures $(P_{-80°}/P_{25°})$ is a relative index of the degree of condensation.

Corrections were made for the pressure increase due to temperature rise alone. In some cases the higher hydrocarbons were oxidized on copper-copper oxide at 540° and the carbon dioxide and water formed were measured. From such data the average formula C_nH_m could be independently calculated. The calculated value of n was normally greater than the observed value owing to solution of higher hydrocarbons in the stopcock grease.

In the condensation processes the quantum efficiency, γ_c, is in every case given by the expression $\gamma_c = (-\Delta CH_4)/tI_{abs}$.

Intensity of light source

A direct measurement of the intensity of light absorbed in the reaction system was made by means of a thermopile-galvanometer system placed immediately behind the reaction vessel receiving light from the source through the acetic acid filter and lens system in its normal position. The thermopile was calibrated with the aid of a standard lamp[9] of the National Bureau of Standards. In this manner it was found that the total light energy normally falling on the system amounted to $3.1 \pm 0.3 \times 10^3$ ergs per cm^2. This was measured with an evacuated cell, with neither mercury vapor nor other gas measurably present. Of the light energy from the arc passed by the acetic acid filter, it was found that 63.6 ± 0.5 percent was the resonance radiation $\lambda = 2537A$. This was equivalent to 3×10^{-11} Einsteins per cc per sec. in the reaction system (1 Einstein $= N_A h\nu$), as calculated from the amount of maximum absorption when there was high mercury and high hydrogen or methane concentrations in the reaction vessel.

TABLE I. *Relation between arc current and light intensity. Hg at $-190°$; cell evacuated; acetic acid filter 25 vol. percent.*

Current (amp.)	Relative Current	Total Energy ergs/cm² ×10⁻³	Relative Intensity of 2537A	Energy of 2537A Percent
4.51	1.00	3.40	1.00	63.2
3.99	0.886	3.22	0.947	—
3.44	0.763	2.96	0.869	—
2.82	0.626	2.61	0.766	—
2.05	0.455	2.03	0.597	64.1
4.48	0.993	3.46	1.035	—

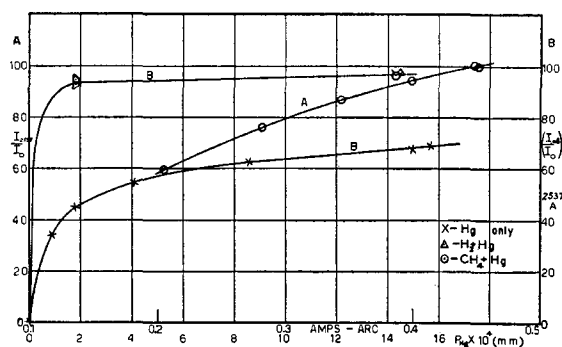[9] A. L. Marshall, J. Chem. Phys. 30, 1085 (1926).

FIG. 2.

The relation between arc current and light intensity is shown in Table I and Fig. 2. The data show that while the total radiant energy emitted falls more slowly than the arc current the fraction of the energy in the form of resonance radiation remains substantially constant.

The chlorine-bromine filter was less efficient. Only 31 percent of the resonance radiation is transmitted by this filter,[9] and spectrographic measurements showed that the acetic acid filter was much superior. Data on the relative rates of the mercury sensitized reaction between hydrogen and oxygen $(2H_2+O_2)$ indicate that the latter filter transmits 83 percent of the resonance radiation, if we assume that the rate of reaction varies directly as the intensity, and that Marshall's figure of 31 percent transmission for this Cl_2-Br_2 cell is correct. With the two filters, Cl_2-Br_2 and acetic acid, the rates of the sensitized reaction $2H_2+O_2$ were 2.8×10^{-11} and 7.6×10^{-11} mole per cc per sec., respectively, at a temperature of 20°. A consumption of approximately 2 mole of $(2H_2+O_2)$ per Einstein absorbed would bring these data into agreement with the thermopile measurements.

Absorption of resonance radiation

A dynamic method was employed to determine accurately the variation of absorbed resonance radiation with mercury pressure in presence and absence of foreign gas. A circulating pump of the Sprengel type was attached to the reaction vessel temporarily to circulate either mercury vapor at controlled vapor pressures or foreign gases at controlled pressures saturated with mercury vapor at controlled temperatures. Circulation was continued until constant absorp-

tions were obtained. The data obtained are exhibited in Table II and graphically in Fig. 2.

It will be noted that the fraction of resonance radiation absorbed rises at first very steeply with the mercury pressure and then more slowly to 0.69 at 15.7×10^{-4} mm Hg pressure. The addition of high pressures of either hydrogen or methane considerably *increases* the fraction absorbed, e.g., from 0.45 to 0.94 with $[Hg]=1.8\times10^{-4}$ mm and $[H_2]=0$ and 142 mm. Since methane is apparently as efficient as hydrogen, the effect cannot be due to quenching and must be attributed to pressure broadening effects.[10] Spectrophotographic measurements of the absorbed radiation gave results entirely concordant with these data.

A static method of measurement of absorption of resonance radiation gives rise to equivocal results. If gas be introduced into the reaction vessel through a trap containing mercury held at the same temperature as the mercury vapor source, the initial concentration of mercury is markedly higher than the saturated vapor pressure at the temperature in question. This is because mercury vapor is introduced by the carrier gas into a space already saturated with mercury vapor. Desaturation occurs only slowly due to the slowness of the diffusion process, and may consume many hours. Advantage may be taken of this to obtain maximum absorption of resonance radiation at room temperatures in the presence of high hydrogen or methane concentrations.*

EXPERIMENTAL RESULTS

I. The exchange reaction

(a) *The effect of temperature and light intensity.*— The data for the effect of temperature, from 98 to 488°, and of light intensity using the Cl_2-Br_2 and acetic acid filters are shown in Table III. The data reveal an increase in quantum efficiency of exchange, γ_e, from 0.6 at $\sim100°$ to 70 at $\sim490°$. The temperature coefficient is not constant but increases from a value $E\sim2$ kcal. in the lower temperature range to

[10] For a contrary point of view not based on absorption measurements see Melville, Proc. Roy. Soc., **A152**, 332 (1935).
* We wish to express our thanks to Dr. N. R. Trenner for assistance in making these thermopile measurements.

14 kcal. in the high temperature range. Both these lines of evidence suggest a chain reaction of exchange increasing in length with increase of temperature.

In the low temperature range a decrease of intensity, I_0, decreases the rate (γ) but at high temperatures the reverse is true. This points definitely to a change of mechanism as the temperature is raised.

(b) *The effect of mercury concentration.*—The data of Table IV with the mercury at its saturation pressure at 0°, 1.8×10^{-4} mm are to be compared with the data of Table III, since in both the acetic acid filter was used. It will be noted that the effect of the lowered mercury concentration is quite similar to the effect of the decreased light intensity when the $Cl_2 - Br_2$ filter was used.

(c) *Comparison of the reactions $CH_4 + D_2$ and $CH_4 + CD_4$.*—The data of Table V show that, in the absence of hydrogen, methane and methane-d_4 undergo exchange reaction. The rate is, however, much slower than in the exchange of methane and deuterium. The effect of temperature is very similar in the two cases and since the activation energy in the case of the two methanes increases from 8 to 15 kcal. in the range from 296 to 488°, a chain mechanism is

TABLE II. *Absorption of resonance line under various conditions. Cell temp. 24°; arc current 4.5 amp.; fraction of energy as $= 2537A = 0.632$.*

TEMP. OF Hg SATUR-ATOR °C	[Hg] mm ×10⁴	FOREIGN GAS mm at 25°	TOTAL ENERGY FALLING ON SYSTEM ergs/cm² ×10⁻³	RESONANCE LINE ABSORBED ergs/cm² ×10⁻³	FRACTION OF RESONANCE RADIATION ABSORBED
−190	0	—	3.07	—	—
+23.1	15.7	—	1.74	1.34	0.690
+16.2	8.6	—	1.86	1.22	0.628
+7.9	4.1	—	2.02	1.06	0.547
0.0	1.8	—	2.20	0.88	0.451
−6.5	0.9	—	2.43	0.65	0.342
+22.5	15.0	—	1.76	1.32	0.679
0.0	1.8	$H_2 = 142$	1.21		
	1.8	$H_2 = 142^1$	1.25	1.83	0.943
	1.8	$H_2 = 142^2$	1.25		
−190	0	—	3.08	—	—
−190	0	—	3.17	—	—
0.0	1.8	$H_2 = 288$	1.31	1.84	0.926
22.1	14.5	$H_2 = 290$	1.21	1.94	0.975
22.0	14.3	$H_2 = 142$	1.22	1.93	0.969
22.0	14.3	$CH_4 = 141$	1.23	1.92	0.963
−190	0	—	3.12	—	—

[1] After 18 min. circulation.
[2] After 33 min. circulation.

indicated in this case also. The small effect of low concentrations of deuterium on the methane-methane-d_4 exchange is also to be noted.

(d) *Comparison of the reactions $CH_4 + D_2$ and $CD_4 + H_2$.*—The rates of these two reactions under comparable conditions are almost identical as shown in Table VI. Indeed, the reaction $CD_4 + H_2$ appears to be somewhat the faster of the two.

(e) *Kinetics of the reaction $CH_4 + D_2$.*—An examination of the effect of various concentration ratios of the two gases at the two temperatures 196 and 392°, as shown in Table VII indicate clearly that the kinetics are different at the two temperatures. The dependence on total pressure, methane and deuterium concentrations shown below the table, is calculated from a very restricted series of measurements and no precision is claimed for the exponents thus secured. They do indicate, however, very varied effects of the three variables in the two temperature regions where the quantum efficiency shows a 12-fold ratio.

(f) *Composition of exchanged methanes produced.*—In the low temperature runs at 98°, the composition of the products deviates considerably from the equilibrium distribution usually attained in the high temperature runs. This is revealed in Table VIII and Fig. 3.

II. The condensation reactions

(a) *The effect of temperature.*—Methane condenses to yield saturated higher hydrocarbons and hydrogen without pressure change under the influence of resonance radiation as revealed by the data of Table IX. At the highest temperature, $\sim$490°, there was a small but definite pressure increase, with production of unsaturated hydrocarbons identified by analysis. The table shows that the extent of condensation, n, decreases with increase of temperature but the rate increases. A composite sample of many runs (Nos. 65–96) showed 3.8 percent unsaturates. The saturated hydrocarbons in the same composite sample were analyzed by fractionation to yield $C_2H_6 \leqq 10$ percent; $C_3H_8 \sim 50$ percent; $C_4H_{10} \sim 39$ percent. The data of Table IX as plotted in Fig. 4 indicate that while the initial rate of condensation progressively increases with increase of temperature the stationary state of

TABLE III. *Effect of temperature and light intensity.* P_{Hg} at $55° = 1.8 \times 10^{-2}$ mm.

No. OF EXPT.	CH_4 cc/25°	D_2 cc/25°	REACTION TEMP. °C	REACTION TIME HRS.	C–D			
					%	cc	cc/hr.	γ
Cl–Br Filter, $I_t = 31\%$, $I = 0.23$ cc/hr.								
10	42.3	42.5	196	30	2.5	4.23	0.14_1	0.61
11	42.0	42.2	196	60	4.0	6.72	0.11_2	0.49
18	43.2	43.1	247	30	7.0	12.1	0.40_2	1.7_6
8	41.9	42.0	296	15.3	8.8	14.7_5	0.96_4	4.2
9	41.9	42.2	296	30	13.5	22.8	0.76	3.3
19	44.0	44.0	344	8.7	13.0	22.9	2.63	11.4
Acetic Acid Filter, $I_t = 83.1\%$, $I = 0.61$ cc/hr.								
91[2]	41.4	41.2	98	113	17.5	29.0	0.25_7	0.42
47[1]	43.3	43.2	98	31.5	6.5	11.3	0.35_9	0.59
14	43.7	43.6	196	12	4.2	7.3_4	0.61_2	1.0
15	43.7	43.6	196	6.5	2.5	4.3_6	0.66_9	1.1
48[1]	43.1	43.3	196	12	4.2	7.2_4	0.60_3	1.0
16	43.5	43.5	247	7.0	4.5	7.8_3	1.1_2	1.8_4
12	43.2	43.2	296	6.5	8.5	15.0	2.3_1	3.8
13	43.7	43.7	296	3.0	5.0	8.7_4	2.9_1	4.8
17	43.5	43.5	344	3.0	8.0	13.9	4.6_8	7.6
21	45.0	44.8	392	2.0	11.0	19.8	9.9	16.2
26	45.9	45.9	392	2.1	13.5	24.8	11.8	$19._4$
25	44.9	44.9	488	0.5	12.0	21.6	43.2	71

[1] Special caution was taken to dry the gas and no effect of water observed.
[2] After separation of higher hydrocarbon, C–D bonds measured.

hydrocarbon production changes with the temperature. Over a period of twenty-four hours illumination the amounts of methane converted to higher hydrocarbons increase up to a temperature of 296°, and decrease with further temperature increase. Table IX also shows that the rate of condensation increases with decrease in the mercury vapor concentration.

Fig. 4 shows that the variation of the rate of condensation with temperature is the opposite of that in the exchange reaction. Increase of temperature produces a marked effect in the low temperature range and a much smaller effect at higher temperatures. In only two cases does the quantum efficiency exceed 2, in both cases at the highest temperature, 488°.

(b) *Kinetics of condensation.*—The data of Table X show that the rate of methane condensation increases with increase in methane concentration, $v \propto [CH_4]^x$ but x decreases progressively with increase of temperature from 0.71 at 196° to 0.28 at 488° (Table XI).

(c) *Effect of H_2 and D_2 on methane condensation.*—The rate of condensation in presence of deuterium is greater than that in presence of hydrogen as Table XII shows. The temperature coefficients are remarkably similar as can be seen

from Fig. 5. They are less than the temperature coefficient in absence of added gas especially in the high temperature range. A remarkable increase in the rate of condensation with added deuterium is found in the low temperature range by decreasing the mercury concentration to the saturated vapor pressure at 0°.

III. General summary of experimental results

For purposes of ready reference in the discussion which succeeds we have collected in Table XIII the mean values for quantum efficiency, γ_e, for the various reactions studied at the various temperatures. Fig. 6.

The apparent activation energies which we calculate from these data are summarized in Table XIV.

DISCUSSION OF RESULTS

IV. General conditions in the reaction system

(a) *Light absorption.*—For a given condition of illumination, in accordance with Beer's law, the ratio I_{abs}/I_0 is constant. The concentration of excited mercury and, hence, *inter alia*, the deuterium atom concentration will be so distributed through the reaction system that they

TABLE IV. *Effect of vapor pressure of mercury. HAc filter.* P_{Hg} *at* $0° = 1.8 \times 10^{-4}$ *mm.*

No. OF EXPT.	CH₄ cc	D₂ cc	REACTION TEMP. °C	REACTION TIME hrs.	C−D %	cc	cc/hr.	γ
97[1]	41.9	41.3	98	1.03	9.2	15.4	0.15	0.25
43	43.1	43.2	196	12.0	2.5	4.31	0.35_3	0.59
44	43.3	43.3	196	12.0	2.5	4.3_3	0.36_1	0.59
45	43.4	43.4	296	6.0	10.0	$17._4$	2.8_9	4.7
46	44.0	43.2	392	2.0	15.0	26.4	13.2	21.6

[1] After separation of higher hydrocarbons, C−D bonds measured.

TABLE V. *Comparison of reaction* $CH_4 + D_2$ *and* $CH_4 + CD_4$. *HAc filter = 0.61 cc/hr.;* $P_{Hg\ 55°} = 1.8 \times 10^{-2}$ *mm.*

No. OF EXPT.	CH₄ cc	D₂ cc	REACTION TEMP. °C	REACTION TIME hrs.	C−D %	cc	cc/hr.	γ
40	43.0	42.8	296	6.0	9.0	17.2	2.87	4.7
21	45.0	45.0	392	2.0	11.0	19.8	9.9	16.2
26	45.8	45.8	392	2.1	13.5	24.7	11.8	19.4
25	44.9	44.9	488	0.5	12.0	21.6	43.1	71
	CH₄	CD₄			Way to eq. nil. %			
24	23.6	23.6	488	4.0	8.8	8.3	0.51_8	3.4
27	23.3	23.3	488	4.0	8.8	8.3	2.0_8	3.4
22	23.6	23.4	392	16.0	8.8	8.2	2.0_5	0.85
28	22.8	22.8	392	13.0	6.5	5.9_3	0.45_6	0.75
29	22.7	22.8	296	48	9.2	8.3_5	0.17_4	0.28
41	{21.3 D₂=4.45	21.6	296	12.0	3.0	2.5_7	0.21_4	0.35
42	{21.3 D₂=1.50	21.4	296	12.0	2.0	1.7	0.14_2	0.23

TABLE VI. *Comparison of reaction* $CH_4 + D_2$ *and* $CD_4 + H_2$. *HAc filter 0.61 cc/hr.;* $P_{Hg\ 55°} = 1.8 \times 10^{-2}$ *mm.*

No. OF EXPT.	CH₄ cc	D₂ cc	TEMP. °C	TIME hrs.	C−D %	cc	cc/hr.	γ
37	43.0	43.0	198	12.0	3.2	5.1_6	0.43	0.71
35	43.0	42.7	296	6.0	7.0	12.1	2.0_1	3.3
40	43.0	42.8	296	6.0	9.0	15.5	2.5_8	4.2
39	42.8	42.7	392	2.0	13.5	23.1	11.5	18.9
	CD₄	H₂			C−H			
36	43.0	43.0	198	12.0	3.5	6.0_2	0.50_2	0.82
33	42.4	42.4	296	6.0	8.5	14.4	2.40	3.9
38	42.9	42.9	392	2.0	14.5	24.9	12.4	20.3

TABLE VII. *Kinetics of* $CH_4 + D_2$. *HAc filter;* $P_{Hg\ 55°}$.

No. OF EXPT.	CH₄ cc	D₂ cc	REACTION TEMP. °C	REACTION TIME hrs.	C−D %	cc	cc/hr.	γ
48	43.1	43.3	196	12.0	4.2	7.25	$.60_4$	1.0
49	21.3	21.4	196	12.0	5.8	4.9_4	$.41_2$	0.68
50	21.7	67.9	196	6.0	3.0	2.6	$.43_3$	0.71
51	43.7	21.7	196	8.7	4.5	7.8_6	$.90_4$	1.5
54	40.3	40.3	392	2.0	10.5	16.9	8.4_6	13.9
55	19.9	20.0	392	2.0	12.5	9.9_5	4.9_8	8.2
56	19.9	60.7	392	2.0	20.5	16.3	8.16	13.4
57	38.3	19.9	392	2.0	6.0	9.2	4.6	7.5

At 196° rate of exchange $\propto (T.P.)^{+2.5} (CH_4)^{-0.5} (D_2)^{-1.5}$ At 392° rate of exchange $\propto (T.P.)^{-3.2} (CH_2)^{+1.5} (D_2)^{+2.4}$

TABLE VIII. *Composition of exchanged methane from 98° runs.*

No. OF EXPT.	TEMP. OF Hg SATURATOR	C−D %	CH₃D% Found	Equil.	CH₂D₂% Found	Equil.	CHD₃% Found	Equil.
47	55	6.5	12	20	7	3	2	neg.
91	55	17.5	25	36	12	14	7	2
97	0	9.2	16	26	6	4.5	3	0.5

will be greatest near the front window, and will decrease exponentially with increasing distance from the window. As the concentration of mercury decreases, the reaction volume increases, thus having the effect of lowering the deuterium atom concentration and that of other decomposition fragments in the reaction volume, even though, as measurements showed, the total absorption of resonance radiation was always close to 100 percent.

(b) *The deuterium atom concentration.*—Farkas and Sachsse have studied in detail[11] the atomic hydrogen concentration in hydrogen-mercury mixtures illuminated by resonance radiation. They found that, with a source of resonance radiation 100 times that used in our investigations the rate of recombination of atoms was $k^1_{H_2} = 3.4 \times 10^{16}$ cm^6 mole^{-2} sec.$^{-1}$, the atomic concentration being given by the expression, $[H] = (2I_{abs}/k^1_{H_2}[M])^{\frac{1}{3}}$. In their experiments diffusion to the wall was negligible above 200 mm total pressure. The rate of recombination of deuterium atoms will be $\sqrt{2}$ times slower or $k^1_{D_2} = 2.4 \times 10^{16}$ cm^6 mole^{-2} sec.$^{-1}$. The D atom concentration, neglecting diffusion, and with our intensity, $I = 3.0 \times 10^{-11}$ Einstein's cm^{-3}

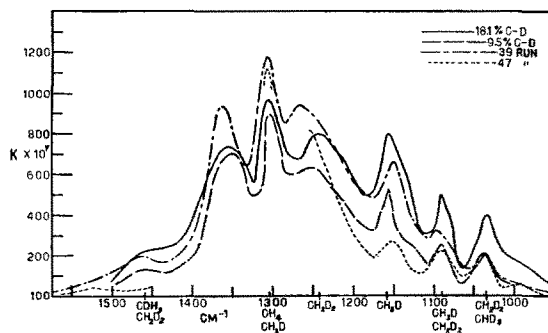[11] Farkas and Sachsse, Zeits. f. physik. Chemie **B27**, 111 (1934).

FIG. 3. Infrared spectra of deuteromethanes produced in low temperature runs.

sec.$^{-1}$, and $[M] = [D_2] + [CH_4] = \sim 13 \times 10^{-6}$ mole cm^{-3}, is calculable from the same equation as 13.7×10^{-12} mole cm^{-3}. These data refer to a mercury saturation at 24°. Correcting, with Farkas and Sachsse, to a saturation temperature of 55° we derive a value $[D] = \sim 4 \times 10^{-12}$ mole cm^{-3}.

Since the mean life of the deuterium atoms is $[D]/2I$ we derive an atom lifetime under our conditions of 6.7×10^{-2} sec. From the diffusion equation $(x^2)_{Av.} = 2Dt$ we deduce that $x_{Av} = \sim 0.6$ cm. This means that the atoms in approximately half the volume of our reaction cell are within diffusion range of the walls during

TABLE IX. *Effect of temperature on production of higher hydrocarbons from methane.* $V = 88$ cc. P_{Hg} at 55°. *Acetic acid filter.* $\gamma = (-\Delta CH_4 \text{ in } cc)/(hrs. \times 0.61)$.

No. OF EXPT.	CH$_4$ mm	REACTION TEMP. °C	REACTION TIME hrs.	RECOV. GAS mm	$-\Delta CH_4$ mm	$-\Delta CH_4$ cc	$+\Delta$ higher h-c mm	$+\Delta H_2$	C_n n	H_m m	$\frac{P_{-80°}}{P_{25°}}$	γ
58	359.0	392	18.5	359.5	43.1	4.9$_9$	14.2		3.0		'	0.43
59	355.6	392	16.0	356.5	40.7	4.71	17.1		2.1			0.48
60	359.1	392	7.0	359.9	33.4	3.8$_7$	16.0		2.1			0.91
61	365.8	392	4.0	366.3	29.0	3.36	12.9		2.3			1.38
62	215.9	392	4.0	216.2	20.7	2.40	9.2		2.3			0.98
66	357.2	196	16.0	357.1	22.3	2.5$_8$	4.9	17.5	4.5	11.1	0.46	0.265
67	359.1	196	35.5	359.2	34.3	3.9$_7$	6.9	28.5	5.0	11.6	0.27	0.184
68	358.2	296	17.1	357.9	43.3	5.0$_2$	10.8	32.6	4.0	10.0	0.45	0.48
69[2]	357.7	296	6.7		29.0	3.36	8.3	20.5	3.5	9.0	0.39	0.82
70[3]	360.8	488	4.0	362.7	26.7	3.09	11.8	16.9	2.3	6.2	0.90	1.27
73	359.2	488	12.4	362.2	35.5	4.1$_1$	15.8	23.3	2.3	6.0	0.92	0.54
79	359.1	196	12.0	359.4	17.5	2.03	3.9		4.5		0.49	0.28
80	359.0	296	3.0	359.1	18.3	2.12	5.8	—	3.2	—	0.69	1.16
84	358.1	488	1.1	359.2	13.7	1.59	6.0	—	2.3	—	0.98	2.6
92	360.2	98	64.5	360.2	2.7	0.31	0.5	—	5.4	—	0.73	0.008
93	357.4	296	3.2	357.9	19.2	2.2$_2$	8.0	—	2.4	—	0.69	1.14
			P_{Hg} at 0°									
95	356.3	196	12	356.4	20.2	2.3$_4$	4.5	—	4.5	—	0.47	0.32
96[1]	354.6	196	9	354.3	14.5	1.6$_8$	3.9	—	3.7	—	0.57	0.31

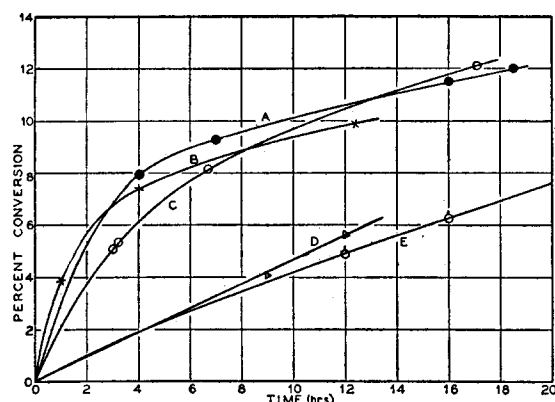[1] I_0 was a little weaker.
[2] By expt. C$_{2.8}$H$_{7.5}$.
[3] By expt. C$_{2.1}$H$_{5.5}$.

FIG. 4. Effect of temperature on the condensation of methane. Curve A, CH_4+H_2, 392°C, Hg at 55°C; V, CH_4+H_2, 488°C, Hg at 55°C; C, CH_4+H_2, 296°C, Hg at 55°C; D, CH_4+H_2, 196°C, Hg at 0°C; E, CH_4+H_2, 196°C, Hg at 55°C.

TABLE XI. *Kinetics of condensation of CH_4. Rate $\infty [CH_4]^x$.*

Temp. °C	x
196	0.71
392	0.46
488	0.28

their mean lifetime. It is obvious, therefore, that under our experimental conditions diffusion cannot be neglected, and at the higher temperatures becomes increasingly prominent, since D varies as $T^{\frac{3}{2}}$. The difficulty of securing uniform temperature in the reaction system also suggests that convection currents will emphasize this effect.

(c) *Calculation of activation energy from the absolute rate of exchange in CH_4+D_2.*—Neglecting any disappearance of atomic deuterium due to such effects we calculate from the atom concentration, that, if the reaction were $CH_4+D = CH_3D+H$, the activation energy at 100° would be 14 kcal. If we assume one order lower atom concentration the activation energy would be 12.5 kcal. Table XIV shows an observed activation energy of 2–3 kcal. We conclude therefore that the exchange reaction at 100° cannot be the simple reaction, $CH_4+D = CH_3D+H$. This is confirmed by our inability to secure this reaction with atomic deuterium from a discharge tube as we shall report later. We are compelled

therefore to look for the mechanism of exchange via fragments of methane, especially CH_3.

(d) *Quenching by methane.*—In spite of the experiments of Bates,[5] much of our work suggests that quenching of excited mercury by methane actually occurs, yielding CH_3 and H as fragments. We call attention to the possibility that this may occur directly and also by collision with metastable mercury atoms.[12] The occurrence of exchange and condensation in methanes rigorously freed from hydrogen and water vapor (I, c) is one such piece of evidence. The negligible influence of small amounts of deuterium on the exchange reaction between the methanes (I, c) at higher temperatures is further evidence that quenching by methane must be an important primary process. The relative rates of exchange in the systems CH_4+D_2 and CD_4+H_2 (I, d) constitute additional evidence. The latter reaction is somewhat faster. If the main reactions were CH_4+D and CD_4+H we would expect the latter to be the slower. If, on the other hand, the main reactions are CH_3+D_2 and CD_3+H_2 we may expect a compensation of effects. Quenching by CH_4 may be faster than by CD_4 but CH_3+D_2 should be slower than CD_3+H_2. The abnormal composition of the deuteromethanes produced at low temperatures (I, f) would not be expected if the exchange reaction proceeded via deuterium atoms and methane but is understandable if the

[12] Melville, reference 10, has considered the role of metastable atoms in the sensitized decomposition of ammonia and ammonia-d_3.

TABLE X. *Effect of concentration of methane on production of higher hydrocarbons. P_{Hg} at 55°. Acetic acid filter.*

No. OF EXPT.	CH_4 mm	REACTION TEMP. °C	REACTION TIME hrs.	RECOV. GAS mm	$-\Delta CH_4$ mm	$-\Delta CH_4$ cc	$+\Delta$ higher h-c mm	$+\Delta H_2$ mm	C_n n	H_m m	$\frac{P_{-80°}}{P_{25°}}$	γ
63	356.1	392	4.0	356.4	25.0	2.90	7.9	17.4	3.2	8.3		1.19
64	202.1	392	4.0	203.0	20.0	2.32	6.1	14.4	3.3	8.4		0.95
65	707.9	392	4.0	708.5	37.0	4.28	13.8	24.4	2.7	7.2		1.76
79	359.1	196	12.0	359.4	17.5	2.03	3.9		4.5		0.49	0.28
81	708.0	196	12.0	708.4	28.5	3.30	6.5		4.3		0.54	0.45
83	703.0	488	1.0	703.9	16.6	1.92	8.1		2.1		1.00	3.15
84	358.1	488	1.0	359.2	13.7	1.59	6.0		2.3		0.98	2.6

TABLE XII. *Effect of H_2 and D_2 on production of higher hydrocarbons. P_{Hg} at 55°. Acetic acid filter.*

No. of Expt.	CH₄ mm	H₂ mm	Reaction Temp. °C	Reaction Time hrs.	−ΔCH₄ mm	−ΔCH₄ cc	+Δ Higher h-c mm	C_n	$\dfrac{P_{-80°}}{P_{25°}}$	γ
71²	357.2	357.7	392	12.3	17.3	2.00	7.9	2.2	0.95	0.27
72	360.9	363.7	392	21.0	16.4	1.90	7.8	2.1	0.95	0.15
74	365.0	365.4	296	17.0	24.7	2.86	6.8	3.6	0.52	0.28
75	358.7	357.9	296	5.9	16.0	1.85	5.2	3.1	0.67	0.51₅
76	359.3	360.7	196	22.5	21.5	2.49	4.4	4.9	0.34	0.18
77	358.0	356.6	196	13.5	15.8	1.83	3.7	4.3	0.43	0.22
78	355.9	352.3	196	17.0	18.0	2.08	3.9	4.6	0.39	0.20
D₂										
85	357.0	371.6	196	12.0	26.7	3.09	5.6	4.7	0.69	0.42
86	359.8	368.8	196	5.0	15.5	1.80	4.3	3.6	0.67	0.59
87	359.4	364.8	296	5.0	23.7	2.75	6.7	3.5	0.61	0.90
88	359.4	355.8	296	3.0	17.5	2.03	5.3	3.3	0.72	1.1₁
89	358.6	360.4	296	17.0	36.7	4.25	9.9	3.7	0.51	0.41
90	358.4	380.9	98	24.1	2.6	0.30	0.9	3.1	0.87	0.02
91¹	358.7	356.3	98	113	6.2	0.7₂	1.1	5.1	0.49	0.01
94	375.4	18.7	98	65	3.2	0.37	0.5	6.4	0.76	0.009
D₂P_{Hg} at 0°										
97¹	364.1	363.6	98	103	39.7	4.60	4.4	9.0?	0.40	0.073
98	357.0	357.0	196	7.0	17.7	2.05	4.4	4.0	0.54	0.48
99	354.9	358.5	196	10.0	22.5	2.61	5.5	4.1	0.48	0.43

¹ After separation of higher hydrocarbons, C—D bonds were measured.
² By expt. C₂.₀H₅.₈, by cal. C₂.₂H₆.₄.

TABLE XIII. *Quantum efficiencies in exchange and condensation reactions.*

Reaction	Reactants	Hg Saturation Temp. °C	Temperature °C 488	392	344	296	247	196	98
Exchange	CH₄+D₂ᵃ	55			11.4	4.2	1.8	0.61	
Exchange	CH₄+D₂ᵃ	55	71	19.4	7.6	4.3	1.8	1.1	0.59
Exchange	CH₄+D₂ᵃ	0		21.6		4.7		0.59	0.25
Exchange	CD₄+H₂	55		20		3.9		0.82	
Exchange	CH₄+CD₄	55	3.4	0.80		0.28			
Condensation	CH₄	55	2.7	2.1		1.4		0.29	0.008
Condensation	CH₄	0						0.32	
Condensation	CH₄+D₂	55				1.4		0.68	0.02
Condensation	CH₄+D₂	0						0.59	0.07
Condensation	CH₄+H₂	55				0.63		0.24	

ᵃ Cl₂—Br₂ filter used; in all other cases, acetic acid filter.

TABLE XIV. *Calculated activation energies (kcal.) in exchange and condensation reactions.*

Reaction	Reactants	Hg Saturation Temp. °C	488	392	344	296	247	196	98
Exchange	CH₄+D₂ᵃ	55			←14→	←11→	→10→		
Exchange	CH₄+D₂ᵃ	55	←—14—→		←——11——→		←——7—→		←—2—→
Exchange	CH₄+D₂ᵃ	0			←——12——→		←——10—→		←——3—→
Exchange	CD₄+H₂	55			←——13——→		←——8—→		
Exchange	CD₄+CH₄	55	←—15—→		←——8——→				
Condensation	CH₄	55	←————3————→				←——8—→	←—13—→	
Condensation	CH₄+D₂	55					←——4—→	←—13—→	
Condensation	CH₄+D₂	0							←—7—→
Condensation	CH₄+H₂	55					←——5——→		

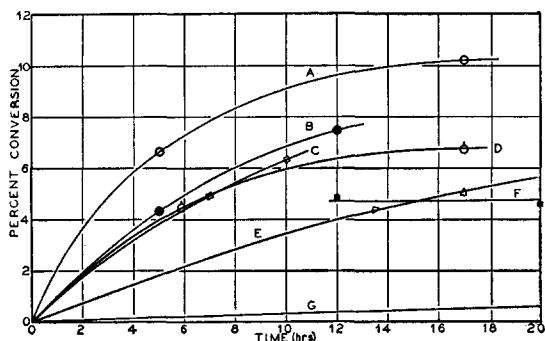ᵃ Cl₂—Br₂ filter used; in all other cases, acetic acid filter.

FIG. 5. Effect of H_2 and D_2 on the methane condensation. Curve A, CH_4+D_2, 296°C, Hg at 55°C; B, CH_4+D_2, 196°C, Hg at 55°C; C, CH_4+D_2, 196°C, Hg at 0°C; D, CH_4+H_2, 296°C, Hg at 55°C; E, CH_4+H_2, 196°C, Hg at 55°C; F, CH_4+H_2, 392°C, Hg at 55°C; G, CH_4+D_2, 98°C, Hg at 55°C.

exchange is between CH_3 and D. Evidence presented in the preceding paper[13] indicates rapid exchange between methyl radicals and atomic deuterium but none below $\sim300°$ between D atoms and CH_4. The increased rate of condensation with decrease of light intensity and mercury concentration as well as the variation in the rate of condensation with temperature (II, a) also point to a primary dissociation to CH_3 and H. The hydrogen atoms diffuse rapidly to the walls and the condensation reaction, involving combination of radicals such as CH_3+CH_3, occurs, in part at least, as a bimolecular association in the gas phase. Our evidence indicates that the recombination CH_3+H as a gas reaction is much less efficient (See V, (f)). From all these lines of evidence we conclude that quenching by methane is an important primary process representable by the equation:

$$CH_4+Hg(^3P_0 \text{ or } ^3P_1) = CH_3+H+Hg,$$
$$CD_4+Hg(^3P_0 \text{ or } ^3P_1) = CD_3+D+Hg.$$
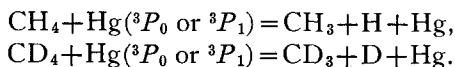
We now consider this conclusion in reference to Bates' observations. From the data of $I(f)$ at 98°, Table VII, expt. 47, on the abnormal distribution of deuterium in the products we conclude that the CH_3 produced is not equal to the C−D exchanged. The excess CH_2D_2 over the equilibrium is $2(7-3)=8$ percent C−D; the excess CHD_3 is $3\times2=6$ percent, an excess in all of 14 percent. The total C−D exchanged is 26 percent. Therefore, it follows that a primary dissociation
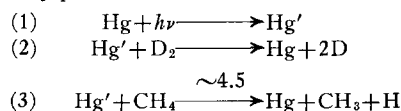
[13] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).

product CH_3 must undergo on the average one exchange, $CH_3+D=CH_2D+H$ before being stabilized.* Therefore, the quantum efficiency γ for expt. 47 should be $0.59/2=0.3$ for the primary dissociation process instead of the observed value. Combining this with the $\gamma=1.1$ at 196° where the ratios of products obey the equilibrium relationships we conclude that the activation energy of the corrected γ is 4.6 kcal. A similar calculation with expt. 97, Table VII, gives ~4.3 kcal. or a mean value of 4.4 kcal. Using this value we calculate a γ at 20° of ~0.086 which is not much greater than would be expected from Bates' quenching data at room temperatures. We suggest, therefore, a quenching efficiency for methane increasing with temperature with an activation energy of ~4.5 kcal.

With methyl radicals as well as hydrogen atom isotopes in the reaction system it is quite evident that the secondary processes are not simple and all possible combinations of methyl radicals, hydrogen atoms and molecules and methane may be involved even in the initial stages and that, in the later stages, higher hydrocarbon molecules and fragments may participate in the mechanisms.

V.

(a) *The possible reactions.*—We classify the possible processes in terms of (a) the primary processes, (b) the secondary processes predominating at lower temperatures, (c) the secondary processes predominating at higher temperatures and (d) later reactions of condensation and decomposition. Our selection is based upon evidence we have accumulated, and are still obtaining, in reference to the occurrence of individual reactions in particular temperature ranges. A broad program of study is in progress designed to yield definitive values for the activation energies of these atom or radical reactions with molecules. The activation energies here cited must be regarded as tentative but in agreement with our best available data.
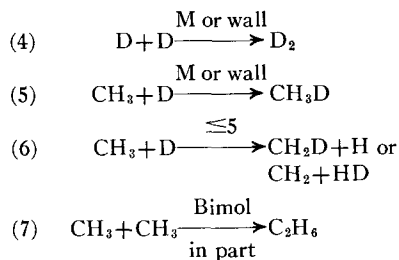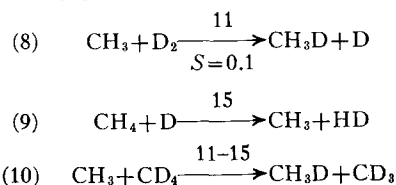
(a) Primary processes

(1) $Hg+h\nu \longrightarrow Hg'$

(2) $Hg'+D_2 \longrightarrow Hg+2D$

(3) $Hg'+CH_4 \overset{\sim4.5}{\longrightarrow} Hg+CH_3+H$

* For the same effect independently observed see reference 13.

(b) Secondary processes at lower temperatures ($<200°$)

$$(4) \quad D+D \xrightarrow{\text{M or wall}} D_2$$

$$(5) \quad CH_3+D \xrightarrow{\text{M or wall}} CH_3D$$

$$(6) \quad CH_3+D \xrightarrow{\leqq 5} CH_2D+H \text{ or } CH_2+HD$$

$$(7) \quad CH_3+CH_3 \xrightarrow[\text{in part}]{\text{Bimol}} C_2H_6$$

(c) Secondary processes in the higher temperature range

$$(8) \quad CH_3+D_2 \xrightarrow[S=0.1]{11} CH_3D+D$$

$$(9) \quad CH_4+D \xrightarrow{15} CH_3+HD$$

$$(10) \quad CH_3+CD_4 \xrightarrow{11-15} CH_3D+CD_3$$

(d) Later reactions of condensation and decomposition

$$(11) \quad C_2H_6+D \xrightarrow{\cdot 11} C_2H_5+HD$$

$$(12) \quad C_2H_5+CH_3 \xrightarrow{\text{Bimol}} C_3H_8$$
$$\text{or} \quad CH_3+CH_2 \longrightarrow C_2H_5$$

$$(13) \quad C_2H_6+D \xrightarrow{\sim7.5} CH_3D+CH_3$$

$$(14) \quad C_2H_6+Hg' \xrightarrow{0} C_2H_5+H+Hg$$
$$\searrow 2CH_3+Hg$$

$$(15) \quad CH_3+CH_4 \xrightarrow{\sim16} C_2H_6+H \text{ (?)}$$
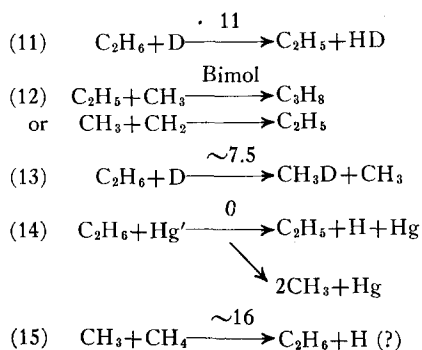
There is some evidence that reaction (15) may occur at temperatures above 400°.

(b) *The mechanisms at various temperatures.*—In the low temperature range, exchange will be mainly by recombination of methyl and atomic deuterium, with exchange also leading to abnormal substitution by reaction (6), which we know to have a low activation energy. The quantum efficiency will be small and determined mainly by the efficiency of (3). Around 200° the exchange by (8) sets in, and only around 300° does reaction (9) become marked.[13] A chain reaction sequence now becomes possible, and hence an increasingly rapid rise in γ.

In the condensation process, recombination of alkyl radicals must be the mechanism whereby higher hydrocarbons are produced. At the low temperatures the primary process (3) will be the sole source of these radicals, and these will be, in the main, methyl radicals only. Other radicals will arise only as the concentration of higher hydrocarbons builds up to measurable quantities.

At sufficiently higher temperatures both methyl radicals and atomic hydrogen or deuterium can be regarded as sources of alkyl radicals, in the case of the atoms by reason of reaction (9). Whether the primary process is methane or hydrogen dissociation at these higher temperatures the maximum potential yield of radicals is two per quantum, unless reactions of the type (15) occur; these might increase the quantum yield slightly beyond 2.

How these mechanisms may be used to interpret the great bulk of the experimental results obtained may now be considered.

(c) *Temperature and the exchange reaction.*—In the low temperature range, reactions (2) to (6) are alone important. The sensitized decomposition of the methane is the rate determining factor and this, as we have shown, has an activation energy of ~4.5 kcal. We anticipate lower observed activation energies than this, since recombination of methyl radicals will decrease exchange and, owing to increased stationary state concentration of methyl, will become more important as temperature increases within the range of temperature in which the secondary
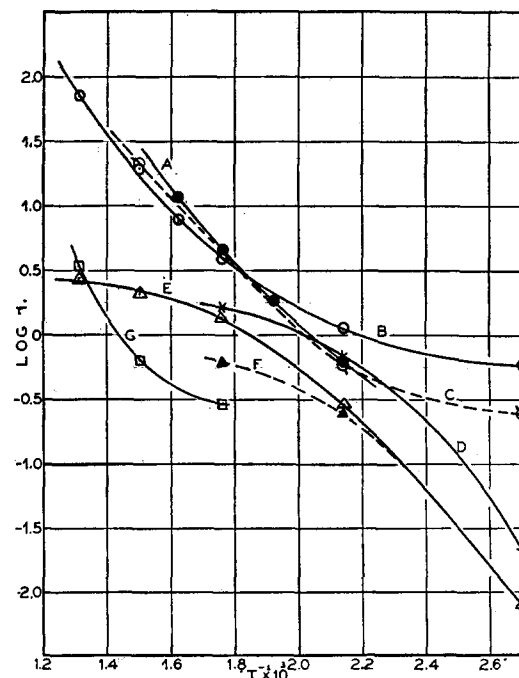

FIG. 6. Exchange: curve A, $CH_4+D_2-Cl_2-Br_2$; B, CH_4+D_2—acetic acid; C, CH_4+D_2, Hg at 0°C. Condensation: D, CH_4+D_2; E, CH_4; F, CH_4+H_2; G, CH_4+CD_4.

chain-producing reactions are not yet markedly occurring. We account thus for the observed values of 2–3 kcal. for the activation energy of exchange in the range 98–196°.

The continuously increasing temperature coefficient from 200° upwards points to the increasing operation of the chain reactions (8) and (9).

(d) *Temperature and the condensation reaction.*—The reverse behavior is to be expected in the case of condensation. Here, at low temperatures, the apparent activation energy is high and decreases steadily with increase of temperature. In the low temperature range this is due to the process of condensation involving the square of the methyl radical concentration, the production of each radical requiring ~4.5 kcal. activation energy. The decrease in temperature coefficient at high temperatures is obviously due to the limitation of quantum efficiency to 2 save for reactions of type (15).

(e) *The kinetics of the exchange reaction.*—The data of (Ie) on kinetics fit closely into the assumed mechanisms especially as to the opposite effects of the total pressure factor at low and high temperatures. At low temperatures, increased total pressure increases atom-radical recombination in the gas phase, therefore favors exchange. At lower total pressures, owing to the faster diffusion of the atoms, more hydrogen atom recombination on the walls will occur and hence more condensation and less exchange. At the higher temperatures, where the chain mechanisms (8) and (9) are predominant, the effect of increased total pressure will be to reduce exchange below what occurs at lower pressures and the same temperature since the three-body recombinations are assisted at the higher pressures at the expense of exchange-producing chain reactions (8) and (9). The negative effects of hydrogen and methane pressures at low temperatures and the positive effects at high temperatures (Ie) are to be interpreted similarly with the mechanisms assumed.

(f) *The relative velocities of CH_4 condensation and $CH_4 - CD_4$ exchange.*—In the temperature range investigated, 296–488°, the condensation process is the more rapid, in spite of its lower temperature coefficient in this range. This can only be explained if we assume that the efficiency of recombinations such as $CH_3 + CH_3$ is much

greater than the atom-radical recombination $H(D) + CH_3$. We conclude therefore that the former approximates more to a bimolecular association reaction than the latter, which appears to require a third body or wall as stabilizer.

(g) *The relative velocities of condensation in $CH_4 + D_2$ and $CH_4 + H_2$ and CH_4 systems.*—Condensation is more rapid in the deuterium-containing than in the hydrogen-containing system. We ascribe this to a higher methyl radical concentration in the system due to a lower rate of reaction of methyl with deuterium than with hydrogen; a higher activation energy for the reaction with deuterium is intrinsically probable.

In the same way, we ascribe the higher velocity of condensation of methane alone over methane-hydrogen mixtures to the influence of greater atomic hydrogen concentration in reducing methyl concentrations in the methane-hydrogen system.

(h) *The effect of light intensity and mercury concentration.*—Decrease of light intensity or of mercury concentration will tend to decrease exchange and increase condensation at the lower temperatures. Both conditions lead to decrease in the stationary state concentrations of methyl and atom. Owing to the more rapid diffusion of atoms to the wall, the wall recombination of hydrogen (3) will be favored, and the exchange reactions (4) and (5) correspondingly decreased. The kinetically more efficient union of two methyl groups will therefore tend to increase, thus accounting for the increase of condensation observed with decrease of mercury concentration at 98°. As the chain-making secondary processes set in this effect of intensity and mercury concentration will disappear due to the increased role which the chain reactions play in the total observed change.

We suggest that the velocity of methane condensation which, at 98°, is smaller than that of $CH_4 + D_2$ mixtures, although the deuterium is an active competitor for the exciting radiation, may be in part due to such causes. The presence of deuterium or hydrogen in the system is equivalent to a decrease in light intensity available for methane dissociation and we may therefore expect an enhancement of condensation to result.

(i) The abnormal distribution of the deutero-methanes at 98°.—At this temperature the main deuteromethane producing process is reaction (5). If the final stabilization is preceded by the formation of unstable quasimolecules CH_3D which dissociate before they can be stabilized, this will tend to give methanes rich in deuterium and an abnormal nonequilibrium distribution of the products. At higher temperatures, the other methane forming processes occurring progressively more rapidly will tend to yield the normal equilibrium distribution of deuteromethanes.

The observed reactions are therefore all satisfactorily interpreted by the sequence of processes postulated. They demonstrate unequivocally in their quantitative aspects the chain character of radical reactions in hydrocarbon-hydrogen (or deuterium) systems at temperatures above 200°. The experimental results are also of importance therefore in pyrolytic reactions which involve hydrocarbon radicals. Further work in progress in this general field will, it is expected, provide still more accurate quantitative data on the velocities of the individual processes.

Raman Spectra of Amino Acids and Related Substances

III. Ionization and Methylation of the Amino Group[1]

JOHN T. EDSALL

Department of Physical Chemistry, Harvard Medical School, Boston, Massachusetts

(Received January 29, 1937)

Raman spectra have been determined for methylated amines, and the corresponding ammonium chlorides in water; also for ethylamine and its hydrochloride, and the hydrochlorides of hydroxylamine, hydrazine and trimethylamine oxide. The spectra of the hydrochlorides arise only from the positively charged ammonium ion, since the chloride ion is not attached by any covalent bond, and, therefore, is not directly involved in any of the observed vibrations. Thus the spectrum of a methylated ammonium ion is found to be exactly similar in type to that of the analogous hydrocarbon in which a C atom is substituted for the positively charged N atom. If the $-CH_3$ and $-NH_3$ groups are treated schematically like single atoms of the same mass, all these compounds may be represented by simple models. The characteristic frequencies of such models may be correlated with lines in the observed spectra. Qualitative polarization measurements have been made on several of the substances studied and have proved of value in assigning observed frequencies to modes of molecular vibration. Bond force constants and valence angles have been evaluated for many of the substances studied, making use of certain approximate potential functions frequently employed in describing systems of this sort. In the solution of hydrazine dihydrochloride, certain Raman lines arise from the ion $^+H_3N \cdot NH_3^+$; others from $^+H_3N \cdot NH_2$. Both ions are present in appreciable concentrations, and their relative amounts are roughly what would be expected from known data on dissociation constants. The Raman spectra of the amines here studied in aqueous solution are nearly identical with those reported by other observers for the same amines as anhydrous liquids. The characteristic valence vibrations of the uncharged amino group, between 3300 and 3400 cm^{-1}, are absent in the charged $-NH_3^+$ or NH_2^+ group, being apparently replaced by much weaker lines of lower frequency. The sodium salts of glycine and alanine show strong Raman lines above 3300 cm^{-1}, which are absent in the isoelectric amino acids. This fact supplies further evidence that the amino acids exist as electrically charged dipolar ions, $^+H_3N \cdot R \cdot COO^-$.

INTRODUCTION

FROM the standpoint of the electronic theory of valence, the positively charged nitrogen atom is an almost exact analog of the carbon atom. The ammonium ion corresponds in structure to methane, the methyl ammonium ion to ethane, the tetramethyl ammonium ion to tetramethyl methane, and so forth. Thus two series of exactly analogous compounds exist.[2]

From the point of view of chemical behavior, this underlying similarity is often obscured, because the ammonium derivatives can exist only in association with suitable anions as salts. The physical properties of the latter are, of course,

---

[1] A preliminary discussion of part of this work has already appeared in Science **84**, 423 (1936).

[2] N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford, 1927). See especially Chapters IV and XIII.